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Analytical Methods for Trace Metals

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Analytical Methods for Trace Metals

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U.S. ENVIRONMENTAL PROTECTION AGENCY
OFFICE OF WATER PROGRAM OPERATIONS

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This course is designed for chemists or technicians of industrial or municipal treatment plants who are required to perform analysis for trace metals. Participants will learn theoretical concepts and will perform a variety of laboratory determinations. Topics will include metal analysis by atomic absorption, flame photometry and volumetric and colorimetric procedures.

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January 1976

ANALYTICAL METHODS FOR TRACE METALS

This course is designed for chemists or technicians who will perform trace metal analyses in industrial or municipal wastewaters and treatment plant effluents. The analyses presented conform to the guidelines required pursuant to Section 304(g) of the Federal Water Pollution Control Act Amendments of 1972.

U. S. ENVIRONMENTAL PROTECTION AGENCY
Office of Water Program Operations
TRAINING PROGRAM

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CHEMICAL ANALYSES

I FEDERAL REGISTER GUIDELINES

A Authority

Section 304(g) Public Law 92-500 required the EPA Administrator to promulgate guidelines establishing test procedures for the analysis of pollutants that would include the factors that must be provided in any certification (section 401) or permit application (section 402). These test procedures are to be used by applicants to demonstrate that effluent discharges meet applicable pollutant discharge limitations, and by the States and other enforcement activities in routine or random monitoring of effluents to verify effectiveness of pollution control measures.

B Establishment

Following a proposed listing there was a period for reply by interested parties. The final rulemaking was published in the Federal Register on October 16, 1973.

C Format

The Guidelines are given in a Table which lists 71 different parameters, the methodology to be used to determine them and the page numbers in standard references where the analytical procedure can be found.

1 Divisions

The 71 parameters are divided as follows: there are 15 general analytical parameters, 28 trace metals, 17 nutrients, anions or organics, 6 physical or biological and 5 radiological.

2 Sources of procedures

The standard references cited as sources of the analytical procedures for these listings are Standard Methods,[1] ASTM, Part 23[2] and the EPA Chemical Methods Manual.[3] Additional sources of procedures are given as footnotes to the Table.

II EPA CHEMICAL METHODS MANUAL

The EPA Chemical Methods Manual was developed for their water quality laboratories using Standard Methods and ASTM as basic references.

A Analytical Procedures

The manual cites page numbers in these two references where the analytical procedures can be found. In some cases, EPA modified methods from these sources or else developed methods suitable for their own laboratories.

B Other Features

For most of the measurements presented in the EPA Chemical Methods Manual, precision and accuracy data from interlaboratory quality control studies are given for the method cited. The manual also contains a section on sampling and preservation. This is in tabular form and contains information on volumes required for analysis, the type of container that can be used, preservation measures and holding times.

III STATUS OF 1974 EPA MANUAL

A Regarding 1973 Guidelines

Some of the methods included in the 1974 EPA Manual are not automatically acceptable for certification or permit requirements. These methods were published in anticipation of proposed additions to the Federal Register Guidelines. When using this 1974 edition, one must first consult the October 16, 1973 Federal Register in the table column which classifies the method(s) approved for a given parameter. Then if the procedure for that specified method is given in the 1974 EPA Chemical Methods Manual, that procedure is acceptable for certification or permit requirements.

B Example of Use

For example, Federal Register parameter no. 52, fluoride, is to be measured using "Distillation-SPADNS." The 1974 EPA Manual has a procedure for fluoride using the cited SPADNS Method with Bellack Distillation, so this procedure is automatically acceptable for certification and permit requirements. On the other hand, the 1974 EPA Manual also has an electrode method for measuring fluoride. Since the Federal Register does not currently list an electrode as an approved method for measuring fluoride, one may not use this method without formal application to do so.

IV METHODS NOT IN 1973 GUIDELINES

A Application to Use

The system for application to use methods not listed in the October 16, 1973 Federal Register is given in that publication. One supplies reasons for using an alternative method to the EPA Regional Administrator through the state agency which issues certifications and/or permits. If the state does not have such an agency, the application is submitted directly to the EPA Regional Administrator.

B Order of Processing

Before approving such applications, the Regional Administrator sends a copy to the Director of the EPA Methods Development and Quality Assurance Research Laboratory (MDQARL). If the Regional Administrator rejects any application, a copy is also sent to MDQARL. Within 90 days the applicant is to be notified (along with the appropriate state agency) of approval or rejection. MDQARL also receives a copy of approval or rejection notifications for purposes of national coordination.

V REQUIRED ANALYSES

Which measurements are to be done and reported depend on the specifications of the individual certifications or permits.

A Mandatory for Secondary Plants

By July 1, 1977 all municipal secondary wastewater treatment plants will be required to measure and report pH, BOD_5 (biochemical oxygen demand), suspended solids, fecal coliform bacteria and flow. Many plants are required to report these now.

B Additional for Secondary Plants

Other measurements which may be required of secondary treatment plants are residual chlorine, settleable solids, COD (chemical oxygen demand), total phosphorus, and the nitrogen series (total N, NH_3-N, NO_3-N, NO_2-N).

C Municipalities and Industries

Beyond these listings, required analyses will depend on the specific situation of municipality and of each industry.

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C Municipalities and Industries

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1 Non-specific

Non-specific measurements to assess overall water quality might be required like acidity, alkalinity, color, turbidity, specific conductance.

2 Organics

Various organic analyses might be relevant such as total organic carbon, organic nitrogen, phenols, oil and grease, surfactants.

3 Metals

Specified metals may be of interest. Currently, the Federal Register lists 28 trace metals in the test procedure guidelines.

4 Others

Cyanide, bromide, chloride, fluoride and hardness are other measurements that might be required of individual industries.

VI METHODOLOGY AND SKILLS

A Methodology

The analytical methods specified in the Federal Register for these measurements range from "wet" procedures using equipment commonly found in most laboratories to procedures requiring sophisticated instruments such as an organic carbon analyzer or an atomic absorption unit.

B Skills

The degree of analytical skills required to perform the analyses likewise varies, as does the cost of having such analyses performed by service laboratories.

VII OTHER ANALYTICAL CONSIDERATIONS

A Sample

The importance of securing a representative sample of the type (grab or composite) specified by the permit cannot be overstressed.

B Record Keeping

Keeping complete and permanent records about the sample is also essential. Such records include conditions when the sample was collected, chain of custody signatures and details and results of analyses.

C Quality Control

Whether the analyses are done in-house or by a service laboratory, an Analytical Quality Control Program should be established. Fifteen to twenty percent of analytical time (cost) should be given to checking standard curves for colorimetry, analyzing duplicate samples to check precision and analyzing spiked samples to check accuracy. Recording precision and accuracy data on quality control charts is an effective method of using such data as a daily check on analytical performance. This can also be done with numbers reported on "blind" samples sent to service labs.

VIII SUMMARY

The October 16, 1973 Federal Register promulgates guidelines establishing test procedures for the analysis of pollutants which might be required for certification (PL 92-500, section 401) or for permits (PL 92-500, section 402). The issue lists page numbers in standard references where procedures can be found to measure the 71 parameters listed. It also sets forth the regulations for application to use methods not cited in the guidelines. The measurements which must be made should be specified by the agency requiring the data. Apparatus and professional skills to do the measurements will vary. Representative samples, complete records and analytical quality control measures are all necessary elements for producing reliable data.

REFERENCES

1 Standard Methods for the Examination of Water and Wastewater, 13th ed., 1971. APHA. New York, New York.

2 Annual Book of Standards, Part 23, Water, Atmospheric Analysis, 1972, ASTM, Philadelphia, Pennsylvania.

3 Methods for Chemical Analyses of Water and Wastes, 1971, EPA, MDQARL, Cincinnati, Ohio.

This outline was prepared by Audrey E. Donahue, Chemist, National Training Center, MPOD, OWPO, USEPA, Cincinnati, Ohio 45268.

Descriptors: Chemical analysis, chemical guidelines, self-monitoring requirements, non-approved analytical methods

METHODOLOGY FOR CHEMICAL ANALYSIS OF WATER AND WASTEWATER

I INTRODUCTION

This outline deals with chemical methods which are commonly performed in water quality laboratories. Although a large number of constituents or properties may be of interest to the analyst, many of the methods employed to measure them are based on the same analytical principles. The purpose of this outline is to acquaint you with the principles involved in commonly-used chemical methods to determine water quality.

II PRE-TREATMENTS

For some parameters, a preliminary treatment is required before the analysis begins. These treatments serve various purposes.

A Distillation - To isolate the constituent by heating a portion of the sample mixture to separate the more volatile part(s), and then cooling and condensing the resulting vapor(s) to recover the volatilized portion.

B Extraction - To isolate/concentrate the constituent by shaking a portion of the sample mixture with an immiscible solvent in which the constituent is much more soluble.

C Filtration - To separate undissolved matter from a sample mixture by passing a portion of it through a filter of specified size. Particles that are dissolved in the original mixture are so small that they stay in the sample solution and pass through the filter.

D Digestion - To change constituents to a form amenable to the specified test by heating a portion of the sample mixture with chemicals.

III METERS

For some parameters, meters have been designed to measure that specific constituent or property.

A pH Meters

pH (hydrogen ion concentration) is measured as a difference in potential across a glass membrane which is in contact with the sample and with a reference solution. The sensor apparatus might be combined into one probe or else it is divided into an indicating electrode (for the sample) and a reference electrode (for the reference solution). Before using, the meter must be calibrated with a solution of known pH (a buffer) and then checked for proper operation with a buffer of a different pH value.

B Dissolved Oxygen Meters

Dissolved oxygen meters measure the production of a current which is proportional to the amount of oxygen gas reduced at a cathode in the apparatus. The oxygen gas enters the electrode through a membrane, and an electrolyte solution or gel acts as a transfer and reaction media. Prior to use the meter must be calibrated against a known oxygen gas concentration.

C Conductivity Meters

Specific conductance is measured with a meter containing a Wheatstone bridge which measures the resistance of the sample solution to the transmission of an electric current. The meter and cell are calibrated according to the conductance of a standard solution of potassium chloride at 25°C, measured by a "standard" cell with electrodes one cm square spaced one cm apart. This is why results are called "specific" conductance.

D Turbidimeters

A turbidimeter compares the intensity of light scattered by particles in the sample under defined conditions with the intensity of light scattered by a standard reference suspension.

IV GENERAL ANALYTICAL METHODS

A Volumetric Analysis

Titrations involve using a buret to measure the volume of a standard solution of a substance required to completely react with the constituent of interest in a measured volume of sample. One can then calculate the original concentration of the constituent of interest.

There are various ways to detect the end point when the reaction is complete.

1 Color change indicators

The method may utilize an indicator which changes color when the reaction is complete. For example, in the Chemical Oxygen Demand Test the indicator, ferroin, gives a blue-green color to the mixture until the oxidation-reduction reaction is complete. Then the mixture is reddish-brown.

Several of these color-change titrations make use of the iodometric process whereby the constituent of interest quantitatively releases free iodine. Starch is added to give a blue color until enough reducing agent (sodium thiosulfate or phenylarsine oxide) is added to react with all the iodine. At this end point, the mixture becomes colorless.

2 Electrical property indicators

Another way to detect end points is a change in an electrical property of the solution when the reaction is complete. In the chlorine titration a cell containing potassium chloride will produce a small direct current as long as free chlorine is present. As a reducing agent (phenylarsine oxide) is added to neutralize the chlorine, the microammeter which measures the existing direct current registers a lower reading on a scale. By observing the scale, the end point of total neutralization of chlorine can be determined because the direct current ceases.

3 Specified end points

For acidity and alkalinity titrations, the end points are specified pH values for the final mixture. The pH values are those existing when common acidity or alkalinity components have been neutralized. Thus acidity is determined by titrating the sample with a standard alkali to pH 8.2 when carbonic acid would be neutralized to $(CO_3)^{=}$. Alkalinity (except for high acidic samples) is determined by titrating the sample with a standard acid to pH 4.5 when the carbonate present has been converted to carbonic acid. pH meters are used to detect the specified end points.

B Gravimetric Procedures

Gravimetric methods involve direct weighing of the constituent in a container. An empty container is weighed, the constituent is separated from the sample mixture and isolated in the container, then the container with the constituent is weighed. The difference in the weights of the container before and after containing the constituent represents the weight of the constituent.

The type of container depends on the method used to separate the constituent from the sample mixture. In the solids determinations, the container is an evaporating dish (total or dissolved) or a glass fiber filter disc in a crucible (suspended). For oil and grease, the container is a flask containing a residue after evaporation of a solvent.

C Combustion

Combustion means to add oxygen. In the Total Organic Carbon Analysis, combustion is used within an instrument to convert carbonaceous material to carbon dioxide. An infrared analyzer measures the carbon dioxide.

V PHOTOMETRIC METHODS

These methods involve the measurement of light that is absorbed or transmitted quantitatively

either by the constituent of interest or else by a substance containing the constituent of interest which has resulted from some treatment of the sample. The quantitative aspect of these photometric methods is based on applying the Lambert-Beer Law which established that the amount of light absorbed is quantitatively related to the concentration of the absorbing medium at a given wavelength and a given thickness of the medium through which the light passes.

Each method requires preparing a set of standard solutions containing known amounts of the constituent of interest. Photometric values are obtained for the standards. These are used to draw a calibration (standard) curve by plotting photometric values against the concentrations. Then, by locating the photometric value for the sample on this standard curve, the unknown concentration in the sample can be determined.

A Atomic Absorption

Atomic Absorption (AA) instruments utilize absorption of light of a characteristic wavelength. This form of analysis involves aspirating solutions of metal ions (cations) or molecules containing metals into a flame where they are reduced to individual atoms in a ground electrical state. In this condition, the atoms can absorb radiation of a wavelength characteristic for each element. A lamp containing the element of interest as the cathode is used as a source to emit the characteristic line spectrum for the element to be determined.

The amount of energy absorbed is directly related to the concentration of the element of interest. Thus the Lambert-Beer Law applies. Standards can be prepared and tested and the resulting absorbance values can be used to construct a calibration (standard) curve. Then the absorbance value for the sample is located on this curve to determine the corresponding concentration.

Once the instrument is adjusted to give optimum readings for the element of interest, the testing of each solution can be done in a matter of seconds. Many laboratories wire recorders into their instruments to rapidly transcribe the data, thus conserving time spent on this aspect of the analysis.

Atomic absorption techniques are generally used for metals and semi-metals in solution or else solubilized through some form of sample processing. For mercury, the principle is utilized but the absorption of light occurs in a flameless situation with the mercury in the vapor state and contained in a closed glass cell.

B Flame Emission

Flame emission photometry involves measuring the amount of light given off by atoms drawn into a flame. At certain temperatures, the flame raises the electrons in atoms to a higher energy level. When the electrons fall back to a lower energy level, the atoms lose (emit) radiant energy which can be detected and measured.

Again standards must be prepared and tested to prepare a calibration (standard) curve. Then the transmission value of the sample can be located on the curve to determine its concentration.

Many atomic absorption instruments can be used for flame emission photometry. Sodium and potassium are very effectively determined by the emission technique. However, for many elements, absorption analysis is more sensitive because there are a great number of unexcited atoms in the flame which are available to absorb the radiant energy.

C Colorimetry

Colorimetric analyses involve treating standards which contain known concentrations of the constituent of interest and also the sample with reagents to produce a colored solution. The greater the concentration of the constituent, the more intense will be the resulting color.

The Lambert-Beer Law which relates the absorption of light to the thickness and concentration of the absorbing medium applies. Accordingly, a spectrophotometer is used to measure the amount of light of appropriate wavelength which is absorbed by the same thickness of each solution.

The results from the standards are used to construct a calibration (standard) curve. Then the absorbance value for the sample is located on this curve to determine the corresponding concentration.

Many of the metals and several other parameters (phosphorus, ammonia, nitrate, nitrite, etc.) are determined in this manner.

VI GAS-LIQUID CHROMATOGRAPHY

Chromatography techniques involve a separation of the components in a mixture by using a difference in the physical properties of the components. Gas-Liquid Chromatography (GLC) involves separation based on a difference in the properties of volatility and solubility. The method is used to determine algicides, chlorinated organic compounds and pesticides.

The sample is introduced into an injector block which is at a high temperature (e.g. 210°C), causing the liquid sample to volatilize. An inert carrier gas transports the sample components through a liquid held in place as a thin film on an inert solid support material in a column.

Sample components pass through the column at a speed partly governed by the relative solubility of each in the stationary liquid. Thus the least soluble components are the first to reach the detector. The type of detector used depends on the class of compounds involved. All detectors function to sense and measure the quantity of each sample component as it comes off the column. The detector signals a recorder system which registers a response.

As with other instrumental methods, standards with known concentrations of the substance of interest are measured on the instrument. A calibration (standard) curve can be developed and the concentration in a sample can be determined from this graph.

Gas-liquid chromatography methods are very sensitive (nanogram, picogram quantities) so only small amounts of samples are required. On the other hand, this extreme sensitivity often necessitates extensive clean-up of samples prior to GLC analysis.

VII AUTOMATED METHODS

The increasing number of samples and measurements to be made in water quality laboratories has stimulated efforts to automate these analyses. Using smaller amounts of sample (semi-micro techniques), combining reagents for fewer measurements per analysis, and using automatic dispensers are all means of saving analytical time.

However, the term "automated laboratory procedures" usually means automatic introduction of the sample into the instrument, automatic treatment of the sample to test for a component of interest, automatic recording of data and, increasingly, automatic calculating and print-out of data. Maximum automation systems involve continuous sampling direct from the source (e.g. an in-place probe) with telemetering of results to a central computer.

Automated methods, especially those based on colorimetric methodology, are recognized for several water quality parameters including alkalinity, ammonia, nitrate, nitrite, phosphorus, and hardness.

VIII SOURCES OF PROCEDURES

Details of the procedure for an individual measurement can be found in reference books. There are three particularly-recognized books of procedures for water quality measurements.

A Standard Methods[1]

The American Public Health Association, the American Water Works Association and the Water Pollution Control Federation prepare and publish "Standard Methods for the Examination of Water and Wastewater."

As indicated by the list of publishers, this book contains methods developed for use by those interested in water or wastewater treatment.

B ASTM Standards[2]

The American Society for Testing and Materials publishes an "Annual Book of ASTM Standards" containing specifications and methods for testing materials. The "book" currently consists of 47 parts.

The part applicable to water was formerly Part 23. It is now Part 31.

The methods are chosen by approval of the membership of ASTM and are intended to aid industry, government agencies and the general public. Methods are applicable to industrial waste waters as well as to other types of water samples.

C EPA Methods Manual[3]

The United States Environmental Protection Agency publishes a manual of "Methods for Chemical Analysis of Water and Wastes."

EPA developed this manual to provide methodology for monitoring the quality of our Nation's waters and to determine the impact of waste discharges. The test procedures were carefully selected to meet these needs, using Standard Methods and ASTM as basic references. In many cases, the EPA manual contains completely described procedures because they modified methods from the basic references. Otherwise, the manual cites page numbers in the two references where the analytical procedures can be found.

IX ACCURACY AND PRECISION

A Of the Method

One of the criteria for choosing methods to be used for water quality analysis is that the method should measure the desired property or constituent with precision, accuracy, and specificity sufficient to meet data needs. Standard references, then, include a statement of the precision and accuracy for the method which is obtained when (usually) several analysts in different laboratories used the particular method.

B Of the Analyst

Each analyst should check his own precision and accuracy as a test of his skill in performing a test. According to the U. S. EPA Handbook for Analytical Quality Control[4], he can do this in the following manner.

To check precision, the analyst should analyze samples with four different concentrations of the constituent of interest, seven times each. The study should cover at least two hours of normal laboratory operations to allow changes in conditions to affect the results. Then he should calculate the standard deviation of each of the sets of seven results and compare his values for the lowest and highest concentrations tested with the standard deviation value published for that method in the reference book. An individual should have better values than those averaged from the work of several analysts.

To check accuracy, he can use two of the samples used to check precision by adding a known amount (spike) of the particular constituent in quantities to double the lowest concentration used, and to bring an intermediate concentration to approximately 75% of the upper limit of application of the method. He then analyzes each of the spiked samples seven times, then calculates the average of each set of seven results. To calculate accuracy in terms of % recovery, he will also need to calculate the average of the results he got when he analyzed the unspiked samples. Then:

$$\% \text{ Recovery} = \left[\frac{\text{Avg. of Spiked}}{\text{Avg. of Unspiked} + \text{Amt. of Spike}} \right] \times 100$$

Again, the individual's % recovery should be better than the published figure derived from the results of several analysts.

C Of Daily Performance

Even after an analyst has demonstrated his personal skill in performing the analysis, a daily check on precision and accuracy should be done. About one in every ten samples should be a duplicate to check precision and about one in every ten samples should be spiked to check accuracy.

It is also beneficial to participate in interlaboratory quality control programs. The U.S. EPA provides reference samples at no charge to laboratories. These samples

serve as independent checks on reagents, instruments or techniques; for training analysts or for comparative analyses within the laboratory. There is no certification or other formal evaluative function resulting from their use.

X SELECTION OF ANALYTICAL PROCEDURES

Standard sources[1, 2, 3] will, for most parameters, contain more than one analytical procedure. Selection of the procedure to be used in a specific instance involves consideration of the use to be made of the data. In some cases, one must use specified procedures. In others, one may be able to choose among several methods.

A NPDES Permits and State Certifications

A specified analytical procedure must be used when a waste constituent is measured:

1 For an application for a National Pollutant Discharge Elimination System (NPDES) permit under Section 402 of the Federal Water Pollution Control Act (FWPCA), as amended.

2 For reports required to be submitted by dischargers under NPDES.

3 For certifications issued by States pursuant to Section 401 of the FWPCA, as amended.

Analytical procedures to be used in these situations must conform to those specified in Title 40, Chapter 1, Part 136, of the Code of Federal Regulations (CFR). The listings in the CFR usually cite two different procedures for a particular measurement. The CFR also provides a system of applying to the EPA Regional Administrator for permission to use methods not cited in the CFR.

B Ambient Water Quality Monitoring

For Ambient Water Quality Monitoring, analytical procedures have not been specified by regulations. However, the selection of procedures to be used should receive attention. Use of those listed in the CFR is strongly recommended. If any of the data obtained is going to be used in connection with NPDES permits, or may be used as evidence in a legal proceeding, use of procedures listed in the CFR is again strongly recommended.

XI FIELD KITS

Field kits have been devised to perform analyses outside of the laboratory. The kit may contain equipment and reagents for only one test or for a variety of measurements. It may be purchased or put together by an agency to serve its particular needs.

Since such kits are devised for performing tests with minimum time and maximum simplicity, the types of labware and reagents employed usually differ significantly from the equipment and supplies used to perform the same measurement in a laboratory.

A Shortcomings

Field conditions do not accommodate the equipment and services required for pretreatments like distillation and digestion. Nor is it practical to carry and use calibrated glassware like burets and volumetric pipets. Other problems are preparation, transport and storage of high quality reagents, of extra supplies required to test for and remove sample interferences before making the measurement, and of instruments which are very sensitive in detecting particular constituents. One just cannot carry and set up laboratory facilities in the field which are equivalent to stationary analytical facilities.

B NPDES Permits and State Certification

Kit methods that thus deviate from standard laboratory procedures are not approved for obtaining data required for NPDES permits or State construction certifications. If one judges that such a method is justifiable for these purposes, he must apply to the EPA Regional Administrator for permission to use it.

C Uses

Even though the results of field tests are usually not as accurate and precise as those performed in the laboratory, such tests do have a place in water quality programs.

In situations where only an estimate of the concentrations of various constituents is required, field tests serve well. They are invaluable sources of information for planning a full-scale sampling/testing program when decisions must be made regarding location of sampling sites, schedule of sample collection, dilution of samples required for analysis, and treatment of samples required to remove interferences to analyses.

REFERENCES

1 Standard Methods for the Examination of Water and Wastewater, 13th Edition. 1971. APHA-AWWA-WPCF, 1790 Broadway, New York, NY 10019.

2 1974 Annual Book of ASTM Standards, Part 31, Water. ASTM, 1916 Race Street, Philadelphia, PA 19103.

3 Methods for Chemical Analysis of Water and Wastes. 1974. U. S. EPA, EMSL, Cincinnati, OH 45268.

4 Analytical Quality Control in Water and Wastewater Laboratories. 1972. U. S. EPA, EMSL, Cincinnati, OH 45268.

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Descriptors: Analysis, Chemical Analysis, Methodology, Wastewater, Water Analysis

SAMPLE HANDLING - FIELD THROUGH LABORATORY

I PLANNING A SAMPLING PROGRAM

A Factors to Consider:

1 Locating sampling sites

2 Sampling equipment

3 Type of sample required

a grab
b composite

4 Amount of sample required

5 Frequency of collection

6 Preservation measures, if any

B Decisive Criteria

1 Nature of the sample source

2 Stability of constituent(s) to be measured

3 Ultimate use of data

II REPRESENTATIVE SAMPLES

If a sample is to provide meaningful and valid data about the parent population, it must be representative of the conditions existing in that parent source at the sampling location.

A The container should be rinsed two or three times with the water to be collected.

B Compositing Samples

1 For some sources, a composite of samples is made which will represent the average situation for stable constituents.

2 The nature of the constituent to be determined may require a series of separate samples.

C The equipment used to collect the sample is an important factor to consider. ASTM[1] has a detailed section on various sampling devices and techniques.

D Great care must be exercised when collecting samples in sludge or mud areas and near benthic deposits. No definite procedure can be given, but careful effort should be made to obtain a representative sample.

III SAMPLE IDENTIFICATION

A Each sample must be unmistakably identified, preferably with a tag or label. The required information should be planned in advance.

B An information form preprinted on the tags or labels provides uniformity of sample records, assists the sampler, and helps ensure that vital information will not be omitted.

C Useful Identification Information includes:

1 sample identity code
2 signature of sampler
3 signature of witness
4 description of sampling location detailed enough to accommodate reproducible sampling. (It may be more convenient to record the details in the field record book).
5 sampling equipment used
6 date of collection
7 time of collection
8 type of sample (grab or composite)
9 water temperature
10 sampling conditions such as weather, water level, flow rate of source, etc.
11 any preservative additions or techniques
12 record of any determinations done in the field
13 type of analyses to be done in laboratory

IV SAMPLE CONTAINERS

A Available Materials

1 glass
2 plastic
3 hard rubber

B Considerations

1 Nature of the sample - Organics attack polyethylene.

2 Nature of constituent(s) to be determined - Cations can adsorb readily on some plastics and on certain glassware. Metal or aluminum foil cap liners can interfere with metal analyses.

3 Preservatives to be used - Mineral acids attack some plastics.

4 Mailing Requirements - Containers should be large enough to allow extra volume for effects of temperature changes during transit. All caps should be securely in place. Glass containers must be protected against breakage. Styrofoam linings are useful for protecting glassware.

C Preliminary Check

Any question of possible interferences related to the sample container should be resolved before the study begins. A preliminary check should be made using corresponding sample materials, containers, preservatives and analysis.

D Cleaning

If new containers are to be used, preliminary cleaning is usually not necessary.

If the sample containers have been used previously, they should be carefully cleaned before use.

There are several cleaning methods available. Choosing the best method involves careful consideration of the nature of the sample and of the constituent(s) to be determined.

1 Phosphate detergents should not be used to clean containers for phosphorus samples.

2 Traces of dichromate cleaning solution will interfere with metal analyses.

E Storage

Sample containers should be stored and transported in a manner to assure their readiness for use.

V SAMPLE PRESERVATION

Every effort should be made to achieve the shortest possible interval between sample collection and analyses. If there must be a delay and it is long enough to produce significant changes in the sample, preservation measures are required.

At best, however, preservation efforts can only retard changes that inevitably continue after the sample is removed from the parent population.

A Functions

Methods of preservation are relatively limited. The primary functions of those employed are:

1 to retard biological action
2 to retard precipitation or the hydrolysis of chemical compounds and complexes
3 to reduce volatility of constituents

B General Methods

1 pH control - This affects precipitation of metals, salt formation and can inhibit bacterial action.

2 Chemical Addition - The choice of chemical depends on the change to be controlled.

Mercuric chloride is commonly used as a bacterial inhibitor. Disposal of the mercury-containing samples is a problem and efforts to find a substitute for this toxicant are underway.

To dispose of solutions of inorganic mercury salts, a recommended procedure is to capture and retain the mercury salts as the sulfide at a high pH. Several firms have tentatively agreed to accept the mercury sulfide for re-processing after preliminary conditions are met.[4]

3 Refrigeration and Freezing - This is the best preservation technique available, but it is not applicable to all types of samples. It is not always a practical technique for field operations.

C Specific Methods

The EPA Methods Manual[2] includes a table summarizing the holding times and preservation techniques for several analytical procedures. This information also can be found in the standard references[1, 2, 3] as part of the presentation of the individual procedures.

VI METHODS OF ANALYSIS

Standard reference books of analytical procedures to determine the physical and chemical characteristics of various types of water samples are available.

A EPA Methods Manual

The Methods Development and Quality Assurance Research Laboratory of the Environmental Protection Agency, has published a manual of analytical procedures to provide methodology for monitoring the quality of our Nation's Waters and to determine the impact of waste discharges. The title of this manual is "Methods for Chemcal Analysis of Water and Wastes."[2]

For some procedures, the analyst is referred to Standard Methods and/or to ASTM Standards.

B Standard Methods

The American Public Health Association, the American Water Works Association and the Water Pollution Control Federation prepare and publish a volume describing methods of water analysis. These include physical and chemical procedures. The title of this book is "Standard Methods for the Examination of Water and Wastewater."[3]

C ASTM Standards

The American Society for Testing and Materials publishes an annual "book" of specifications and methods for testing materials. The "book" currently consists of 33 parts. The part applicable to water is a book titled, "Annual Book of ASTM Standards, Part 23, Water; Atmospheric Analysis".[1]

D Other References

Current literature and other books of analytical procedures with related information are available to the analyst.

E NPDES Methodology

When gathering data for National Pollutant Discharge Elimination System report purposes, the analyst must consult the Federal Register for a listing of approved analytical methodology. There he will be directed to pages in the above cited reference books where acceptable procedures can be found. The Federal Register also provides information concerning the protocol for obtaining approval to use analytical procedures other than those listed.

VII ORDER OF ANALYSES

The ideal situation is to perform all analyses shortly after sample collection. In the practical order, this is rarely possible. The allowable holding time for preserved samples is the basis for scheduling analyses.

A The allowable holding time for samples depends on the nature of the sample, the stability of the constituent(s) to be determined and the conditions of storage.

1 For some constituents and physical values, immediate determination is required, e.g. dissolved oxygen, pH.

2 Using preservation techniques, the holding times for other determinations range from 6 hours (BOD) to 7 days (COD). Metals may be held up to 6 months.[2]

3 The EPA Methods Manual[2] includes a table summarizing holding times and preservation techniques for several analytical procedures. This information can also be found in the standard references[1, 2, 3] as part of the presentation of the individual procedures.

4 If dissolved concentrations are sought, filtration should be done in the field if at all possible. Otherwise, the sample is filtered as soon as it is received in the laboratory. A 0.45 micron membrane filter is recommended for reproducible filtration.

B The time interval between collection and analysis is important and should be recorded in the laboratory record book.

VIII RECORD KEEPING

The importance of maintaining a bound, legible record of pertinent information on samples cannot be over-emphasized.

A Field Operations

A bound notebook should be used. Information that should be recorded includes:

1 Sample identification records (See Part III)

2 Any information requested by the analyst as significant

3 Details of sample preservation

4 A complete record of data on any determinations done in the field. (See B, next)

5 Shipping details and records

B Laboratory Operations

Samples should be logged in as soon as received and the analyses performed as soon as possible.

A bound notebook should be used. Preprinted data forms provide uniformity of records and help ensure that required information will be recorded. Such sheets should be permanently bound.

Items in the laboratory notebook would include:

1 sample identifying code
2 date and time of collection
3 date and time of analysis
4 the analytical method used
5 any deviations from the analytical method used and why this was done
6 data obtained during analysis
7 results of quality control checks on the analysis
8 any information useful to those who interpret and use the data
9 signature of the analyst

IX SUMMARY

Valid data can be obtained only from a representative sample, unmistakably identified, carefully collected and stored. A skilled analyst, using approved methods of analyses and performing the determinations within the prescribed time limits, can produce data for the sample. This data will be of value only if a written record exists to verify sample history from the field through the laboratory.

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Descriptors: On-Site Data Collections, On-Site Investigations, Planning, Handling, Sample, Sampling, Water Sampling, Surface Waters, Preservation, Wastewater

ATOMIC ABSORPTION SPECTROPHOTOMETRY

I INTRODUCTION

Atomic absorption spectroscopy has been well known to physicists and astronomers for more than 100 years. In 1850, Kirchoff took light from the sun and collimated it with a lens through the flame of an ordinary laboratory burner, and then passed the light through a prism which dispersed it into the characteristic visible spectrum with which we are all familiar. He then took a platinum spoon containing a sodium salt and introduced it into the flame. He observed that the yellow light that was present in the spectrum disappeared and in its place appeared the characteristic resonance lines of sodium. Since then astronomers have used the technique to detect and measure the concentration of metals in the vapors of stars. In 1953, Walsh[1] recognized its potential advantage over emission spectroscopy for trace metal analysis. He designed and built an analytically useful atomic absorption instrument. Shortly thereafter the advantages of atomic absorption instrumentation were recognized in the United States.

II THEORY

The basis of the method is the measurement of the light absorbed at the wavelength of a resonance line by the unexcited atoms of the element. Elements not themselves excited to emission by a flame may be determined in a flame by absorption provided that the atomic state is capable of existence.

At the temperature of a normal air-acetylene flame (2100°C) only about one per cent of all atoms is excited to emission in a flame; therefore absorption due to a transition from the ground electronic state to a higher energy level is virtually an absolute measure of the number of atoms in the flame, and the concentration of the element in the sample. Electrons will absorb energy at the same characteristic wavelength at which they emit energy. This is the principle upon which the technique of atomic absorption spectroscopy is based.

The advantages of atomic absorption spectroscopy as compared to emission spectroscopy are: (1) that atomic absorption is independent of the excitation potential of the transition involved and (2) that it is less subject to temperature variation and interference from extraneous radiation and interference from extraneous radiation or energy exchange between atoms.

Atomic absorption analytical apparatus (Figure 1) consists of a suitable source of light emitting the line spectrum of an element, a device for vaporizing the sample, a means of line isolation (monochomator or filter) and photoelectric detecting and measuring equipment.

If the detector is placed to receive only the resonance line of the element from the light source, measurement can be made of the absorption of resonance-line radiation on its passage through the vaporized sample. The magnitude of this absorption gives a measure of the concentration of free ground-state atoms of the element in the vapor and when referred to a calibration curve, provides a means of determining the concentration of the element in the sample.

III INSTRUMENTATION

The general arrangement of an absorption flame photometer is no different from an emission flame photometer except for the addition of a light source. An aerosol is introduced into a flame which is placed on the optical axis between the entrance slit of the monochromator and the monochromatic light source. Energy of the wavelength absorbed by the sample is provided by a source lamp whose emitting cathode is made of that element. This energy is passed through the flame and then through a dispersing device. A detector measures the absorbed and unabsorbed exciting radiation.

A Light Source

For the more volatile elements such as the alkali metals, mercury and thallium,

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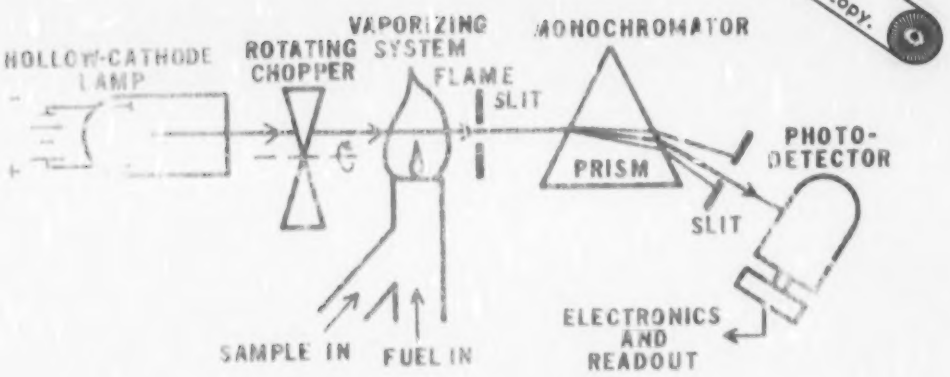

FIGURE 1

the most convenient source is the spectral vapor lamp, which consists of a closed glass or silica tube, into which are sealed oxide-coated electrodes, containing one of the rare gases and some of the appropriate metals. For line sources of the less-volatile elements, hollow-cathode discharge tubes have been found the most satisfactory. These consist of an anode and hollow cylindrical cathode (either composed of or lined with the appropriate metal) mounted in a sealed glass tube containing one of the rare gases (helium or argon).

Lamps are operated at low currents to improve linearity of response and maintain narrow emission lines.

ii Vaporization of Sample

1 Atomic-absorption methods have been applied almost exclusively to the analysis of solutions and for this purpose flames, fed with a fine spray of the sample solution, similar to those employed in flame photometry are used.

The burner has two principal functions to perform:

a It must introduce the sample into the flame.

b It must reduce the metal to the atomic state.

2 Burners can be classified as:

a Total-consumption

Those which introduce the sample spray directly into the flame. (Figure 2)

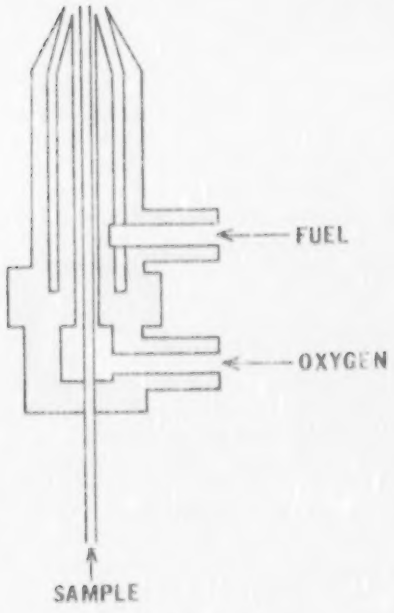

FIGURE 2

b Premix

Those which introduce the spray into a condensing chamber for removing large droplets. (Figure 3)

3 Flame shape is important. The flame should have a long path length (but a narrow width, such as a fishtail flame) so that the source traverses an increased number of atoms capable of contributing to the absorption signal.

4 The effective length of the flame may be increased by multiple passages through the flame with a reflecting mirror system, or by alignment of several burners in series.

5 The flame temperature need only be high enough to dissociate molecular compounds into the free metal atoms.

Typical flame temperatures are shown in Table I.

Table I

Fuel-Oxidant	Approximate Temp., °C
Nitrous Oxide - acetylene	3000
Hydrogen - air	2100
Hydrogen - oxygen	2700 - 2800
Acetylene - oxygen	3100
Acetylene - air	2000 - 2200
Propane - oxygen	2700 - 2800
Illuminating gas - oxygen	2800
Cyuncgen - oxygen	4900

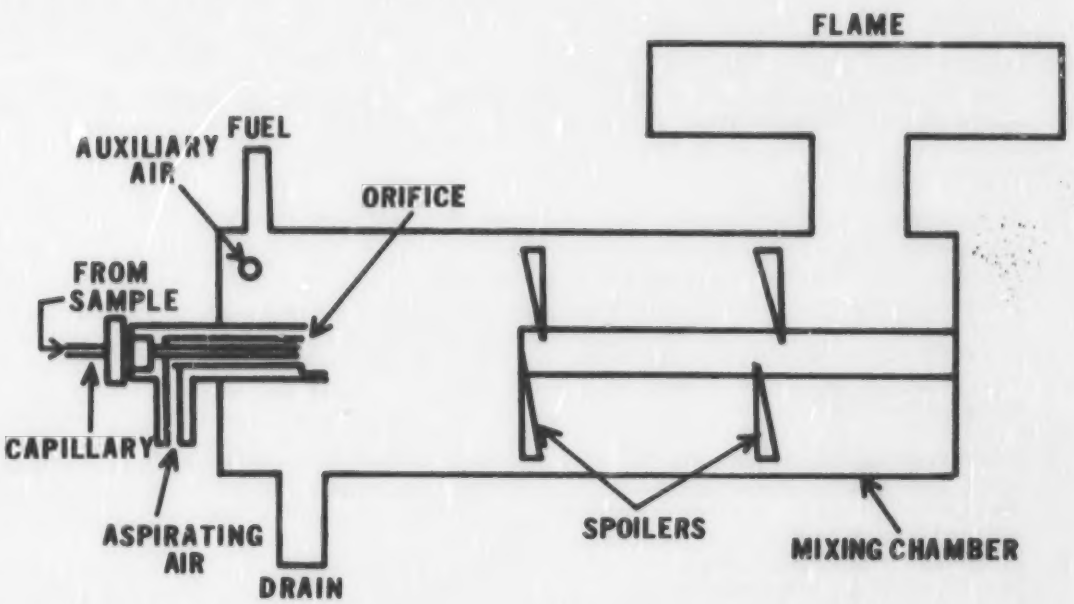

Figure 3

C Line Isolation

1 The use of a line spectrum of the element being determined, rather than a continuous spectrum, makes possible the use of monochromators of low resolving power or even filters. When a spectral lamp is used as a light source, it is only necessary to isolate the resonance line from neighboring lines of the light source or vaporized sample. The resolution of the method is implicit in the width of the emission and absorption lines.

2 To realize the full potentialities of the method, the strongest absorption line must be used. For elements with simple spectra, the resonance line arising from the lowest excited state is usually the line exhibiting strongest absorption.

3 Calibration curves depart from linearity at much lower concentrations in absorption work as compared with emission work. Curvature results partly from increased pressure broadening as the concentration of salt rises, but also depends on source characteristics, particularly self-absorption, and on the nature and homogeneity of the flame.

D Detection

1 Photo-electric detectors used in atomic absorption analysis need be no more sensitive than those used in emission analysis, since in the atomic absorption method, concentration of an element is determined by measuring the reduction in intensity of the resonance line emitted from a source of high intensity.

2 Single or double-beam circuits may be adopted for work with a single beam instrument, results are directly dependent upon source and detector stability. Both must be powered by separate power supplies. In a double-beam system small variations in the source signal are compensated automatically.

IV EVALUATION

A Sensitivity

1 For an air-acetylene flame of length 2 or 3 cm the lower limits of detection of elements having low resonance-line excitation potential (eg Na-K) are approximately equal in a single-beam atomic absorption and emission methods.

2 For elements having highly reversed resonance lines or resonance lines of high excitation potential, the atomic-absorption method has decided advantages over emission methods. Examples of elements in these categories are Zn, Mg, Fe and Mn.

3 A disadvantage of the atomic-absorption method, when compared with flame emission, is the lack of a quick and simple method of varying sensitivity to deal with solutions of widely varying element concentrations. The sensitivity of an atomic-absorption instrument is determined almost entirely by flame characteristics, notably length of light path through the flame.

4 A comparison of sensitivity obtained by emission and adsorption techniques is given in Table II.

B Precision

1 Precision of a single-beam atomic absorption instrument is primarily a function of the stability of light output from the spectral lamp. This in turn is dependent on the stability of the main supply and inherent stability of the lamp. The largest fluctuations are only $\pm$ 2 percent for the hollow cathode tube and sodium spectral vapor lamp. A double-beam instrument significantly reduces this error.

2 In common with flame-emission methods, atomic absorption is subject to "noise" from the flame and the detector. Changes in absorption caused by fluctuations in

Element	Sensitivity mg/l Flame	A.A
Aluminum	2	0.5
Antimony		0.2
Arsenic		1.0
Barium	0.3	1.0
Beryllium	25	0.05
Bismuth		0.2
Cadmium	2	0.01
Calcium	0.003	0.01
Cesium		0.05
Chromium	0.1	0.01
Cobalt		0.15
Copper	0.01	0.005
Gallium		1.0
Gold		0.1
Imdium		0.5
Iron	0.2	0.05
Lead	2	0.15
Lithium	0.002	0.005
Magnesium	0.1	0.003
Manganese	0.01	0.01
Mercury	10	0.5
Molybdenum		0.2
Nickel		0.05
Palladium		1.0
Platinum		0.5
Potassium	0.001	0.005
Rhodium		0.3
Rubidium		0.02
Selenium		1.0
Silver	0.05	0.02
Sodium	0.002	0.005
Strontium	0.01	0.02
Tellurium		0.5
Titanium		1.0
Thallium		0.2
Tin		2.0
Vanadium		0.5
Zinc	200	0.005

Table II

flame temperature are much less than those in emission because the strength of the absorption line is principally dependent on Doppler width whereas the intensity of emission from the flame is much more sensitive to temperature.

C Accuracy

This is shown by the types of interference found in flame emission and atomic absorption spectroscopy. There are three types:

1 Physical

Collision of atoms and electrons or atoms and molecules will transfer energy thus causing an enhancement or depression of analysis-line emission. This has a large effect on flame emission analysis but has only a negligible effect on atomic absorption.

2 Radiative

Light from elements other than the one being measured pass the line isolating device (monochromator or filter). This occurs in flame emission work, for example, the interference of calcium and magnesium in sodium determinations. This interference is also encountered in atomic absorption using a D.C. system but is very small because of the large signal from the hollow-cathode tube. Radiative interference is eliminated in an A.C. system.

3 Chemical

Emission from an element in the flame is depressed by the formation of compounds, which are not dissociated at flame temperatures. This also affects absorption because the formation of temperature - stable compounds in the flame causes proportionate reduction in the population of ground-state and excited atoms.

Investigations to date suggest chemical interference is confined, almost entirely, to the alkaline-earth elements and that calcium absorption is more subject to this interference than is magnesium absorption.

Typical calibration curves are shown in Figure 5.

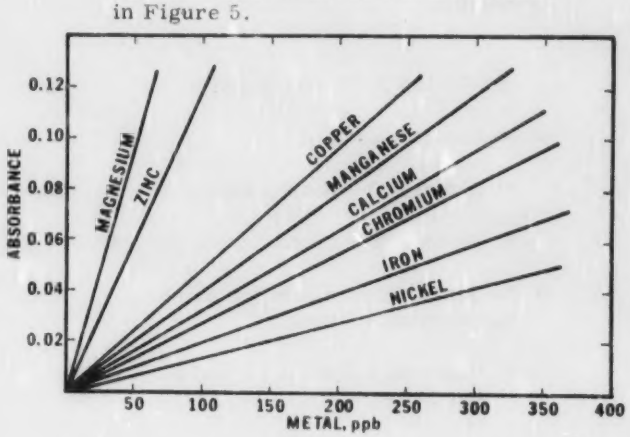

Figure 5

V REMOVAL OF INTERFERENCES AND CONCENTRATION OF SAMPLE

A Removal of Interferences

1 The methods for overcoming these interferences in atomic absorption are similar to those used in flame emission, namely, either separation of interfering ions or suppression of the interference by addition in excess of a substance that will prevent formation of compounds between interfering ions and the element being determined.

B Concentration of Sample

1 Organic separations can be used to concentrate a sample. Interferences are removed, as seen above, and also the organic solvent enhances the absorption.

2 Ion exchange has also been used successfully for concentrating samples for atomic absorption.

VI CONCLUSIONS

Atomic absorption methods are as good as or better than emission methods, for elements to which they can both be applied, in sensitivity, precision and accuracy. They can be applied to a far wider range of elements than can emission analysis. The additional cost of hollow cathode discharge tubes is compensated by the greater range of analyses and greater reliability of results.

VII INSTRUMENTS AVAILABLE

A Perkin Elmer

1 Model 303 - double beam, AC - $5,920.00

1 Model 290 - single beam, AC - $2,900.00

B Beckman attachments for existing spectrophotometers

1 Use with model D.U. and D.U.-2- single beam, DC - $2,135.00

2 Use with model D.B. - single beam, AC - $2,495.00

C Jarrell-Ash

1 Dual atomic absorption flame spectrometer- single beam, AC - $5,800.00

D E.E.L.

1 Atomic absorption spectrophotometer - single beam, AC - $2,850.00

ACKNOWLEDGEMENT

Certain portions of this outline contain training meterial from a prior outline by Nathan C. Malof.

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This outline was prepared by P. F. Hallbach, Chemist, National Training Center, MOTD, OWPO, USEPA, Cincinnati, Ohio 45268.

Descriptors: Analytical Techniques, Atomic Absorption, Instrumental Analysis, Metals Analysis

ENERGY SOURCES FOR ATOMIC ABSORPTION SPECTROSCOPY

I INTRODUCTION

The basic principle behind atomic absorption spectroscopy can be said to be opposite that of emission methods. In emission spectroscopy the sample is raised to a meta stable excited energy level by an input of energy. Then the sample is allowed to return to its stable ground state. When the sample returns to its ground state energy is given off and a high proportion of this energy is at a wavelength characteristic of the metal in the sample that is being analyzed.

In atomic absorption the element under investigation is not excited but is merely dissociated from its chemical bonds, and in an unexcited ground state. It is then capable of absorbing radiation at a characteristic wavelength, i.e., the same wavelength as would be emitted if the element were excited.

This difference affects both the sensitivity and stability of results obtained in analyzing for elements via atomic absorption. Due to the fact that, even at optimum conditions in emission spectroscopy, for every atom available in an excited state there are many more available in the unexcited state. For example, for every calcium atom in the excited state there are about a thousand dissociated and accessible to atomic absorption. For zinc the ratio is even greater, for every one atom that is excited there are 10^9 available for atomic absorption.

These numbers do not indicate a direct proportional increase in sensitivity. Some increase is noticed but not as large as the numbers indicate. In addition to the sensitivity increase, an increase in the stability is also obtained. If during analysis of zinc by emission spectroscopy a change in flame would make available another atom, a change of 100% in the emission value has occurred but the change in atomic absorption would not be significant.

In order to provide energy that the unexcited atoms are capable of absorbing, a hollow cathode lamp is used in atomic absorption. Hollow cathode lamps are manufactured by several firms and the shape of the lamp has little to do with its function. Basically, a hollow cathode lamp is composed of an anode, cathode, shielding, envelope, end window and a filler gas.

To provide energy at the specific wavelength needed for the element under analysis the hollow cathode lamp has its cathode constructed from or lined with the element of interest usually in the shape of a cylinder closed at one end. As each lamp emits the line spectra of the element present in its cathode, a different lamp is usually used for each element analyzed.

Each hollow cathode lamp operates under the same general principle. The lamp envelope is filled with an inert gas, usually argon or neon, at a low pressure (1 to 10 mm Hg). Once sufficient voltage is applied across the electrodes within the lamp, the inert gas ionizes and current begins to flow. When this happens positive gas ions bombard the cathode and heating occurs. As the inner surface of the cathode heats, it sputters and metal vapor fills the cathode volume. Charged gas particles collide with the metal atom, raising its valence electrons to higher energy states. When these excited electrons return to their ground state, they emit light. The spectrum thus emitted contains the same wavelengths of light required for absorption by that metal atom under analysis. As many cathodes are alloyed to obtain mechanical strength and as the gas fill is also excited, the emission of a hollow cathode lamp contains the spectra of more than one element.

Another step to increase the usefullness of a hollow cathode lamp was to incorporate more than one element into the cathode so the lamp could be used for more than one element. This has been done and there are available lamps that contain as many as six elements. Not all elements can be usefully combined in multi-element lamps.

Some combinations are difficult or impossible from a metallurgical viewpoint. More important to the user, some combinations, though feasible to manufacture, yield spectral interferences. Here the emission lines from one element lie

too close to those of another element, so that spurious absorption signals can results, if the second element is also present in the sample.

When three or more elements are combined in a lamp, it is also frequently true that the emission from the individual elements is not as bright as that from single-element lamps. However, one chief advantage lies in the cost. A multi-element lamp is not proportionately as expensive as a single-element lamp. Also, the curves of absorbance versus concentration obtained with multi-element lamps may be less linear than those from single element sources, particularly at high absorptions.

The operating current of a hollow cathode lamp can be a critical parameter in optimizing an atomic absorption measurement. Lamp intensities and resulting absorbance in the flame do not change linearly with operating current. Typically high absorbance and good signal-to-noise ratios are obtained at current near one-third the maximum lamp currents. Increasing the hollow cathode lamp current will increase its output intensity. But sensitivity is reduced through line broadening and/or self reversal for some elements. As a result, we can expect better sensitivity at lower lamp currents.

Most manufacturers will provide a rated maximum current beyond which the lamp should not be operated. Any operation above this current produces the danger of destruction of the cathode. It is best to follow the manufacturer's suggested operational current when using its lamp. If warm-up of the lamp is necessary, as in a single beam spectrophotometer this can be done at currents below the operating current, bringing the lamp to proper current just before use. Lamp current will affect lamp life. Experimental data have shown that lamp life is reduced by the square of the current increase. Thus, lower lamp current can only improve the performance and life of a hollow cathode lamp.

Each hollow cathode lamp will have a different warm-up time which can vary from 5 to 20 minutes. Use of a lamp in a single beam instrument will require a warm-up time but a double beam instrument does not require this waiting period. The use in some instruments of multiple-lamp turret assembly facilitates the operation of many lamps at different operating currents to speed the time of analysis by eliminating warm-up time when lamps are changed. In single beam instruments a multi-element lamp is attractive because all its elements are ready when one element is ready.

Lamp life is hard to estimate; however, most manufacturers guarantee their lamps for a use period of five ampere hours. When this figure is divided by typical operating currents, the average guarantee extends to between 300 and 500 hours of use. In practice, most lamps last a great deal longer. If lamps are not used regularly, it is wise to operate them for at least one hour per month on normal current in order to reduce the possibility of fluctuation when the lamp is finally put into use.

II SUMMARY

In atomic absorption spectroscopy, the hollow cathode lamp is perhaps the most important component. The usefulness of a given analysis depends directly on the brightness, spectral purity and stability of the lamp. Also, the economic feasibility of owning atomic absorption equipment is often closely tied to hollow cathode lamp life.

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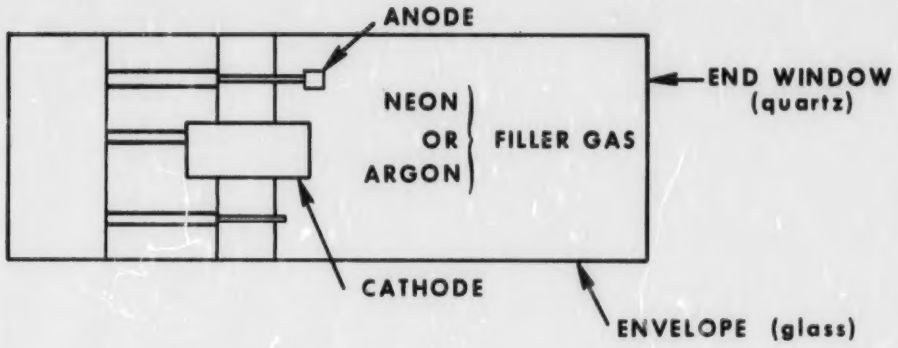


HOLLOW CATHODE LAMP
FIGURE 1

This outline was prepared by J. D. Pfaff, National Training Center, MOTD, OWPO, USEPA, Cincinnati, Ohio 45268.

Descriptors: Spectroscopy, Spectrophotometers

PRINCIPLES OF ABSORPTION SPECTROSCOPY

I INTRODUCTION

In any system employing principles of absorption spectroscopy, there are three basic components.

A SOURCE of Radiant Energy

B MEDIUM (Sample) which absorbs Radiant Energy

C DETECTOR to measure the Radiant Energy transmitted by the Sample

Figure 1. Basic Components of Absorption Spectroscopy System

II RADIANT ENERGY

A Wave Nature

1 The various forms of radiant energy have been arranged in a single schematic diagram referred to as the electromagnetic spectrum (see Figure 2). All of the energies which make up this spectrum may be represented graphically as waves. All waves move through space (and for most purposes air) at a constant velocity, 3×10^{10} cm/sec.

2 Three variable characteristics of individual waves serve to differentiate each from all other waves in the spectrum.

a The Wave Length

λ - The linear distance between the crests of two adjacent waves. (Units: distance/wave.)

b The Frequency

ν - The number of waves which pass a given point in a unit of time. (Units: waves/time unit.)

c The Wave Number

$\bar{\nu}$ - The number of waves which occur in a given linear distance. (Units: waves/distance unit.)

2 It is evident that more waves of short wavelength will "fit" into a given linear distance than would waves of a greater wavelength. Thus, waves having short wavelengths will have higher wave numbers. Mathematically, wave length is the reciprocal of wave number, if the same units of linear measurement are used in each expression. Since the velocity of all waves is equal and constant, it is also apparent that a greater number of waves of short wavelength can pass a given point in a unit of time than waves having a longer wavelength.

B Particle Nature

Planck conducted certain experiments which indicated that light has a particle as well as a wave nature. Energy rays can be said to consist of particles with a definite amount of energy. These particles or packets are referred to as photons or quanta. The energy (E) of each minute packet is given by Planck's equation.

$$E = h\nu \qquad (5)$$

Where E = Radiant Energy in ergs

h = Planck's proportionality constant (6.6×10^{-27} erg sec.)

ν = Frequency in waves per second

Thus, it can be seen that the energy of a given photon is directly proportional to the frequency of the given Radiant Energy.

III ABSORPTION OF ENERGY BY ATOMS AND MOLECULES

A Absorption of energies of given frequencies by atoms and molecules can be used as a basis for their qualitative identification. Absorption spectroscopy is based on the principle that certain displacements of electrons or atoms within a molecule are permissible according to the quantum theory. When radiant energy of the same energy required to bring about this permissible change is supplied to the molecule, the change occurs and energy is absorbed.

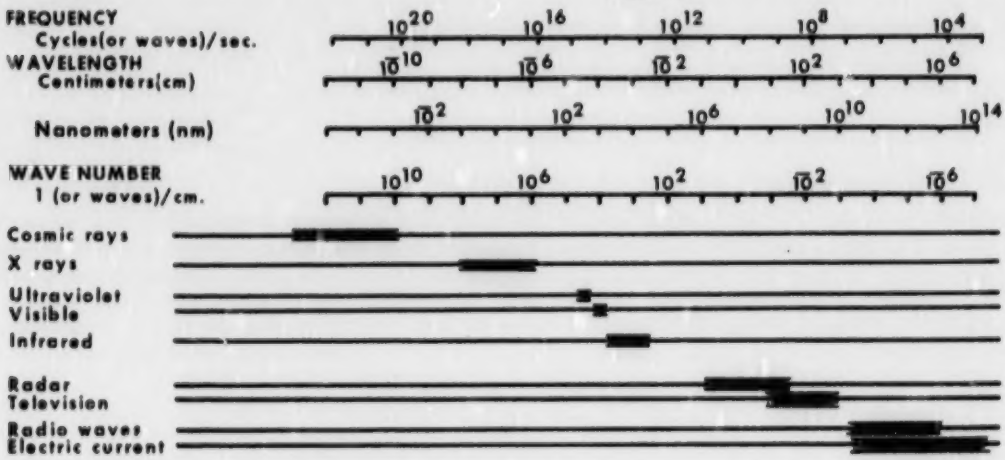
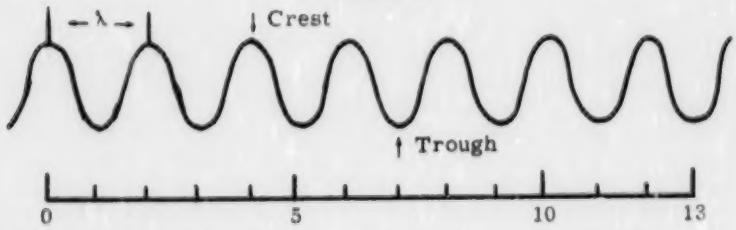


FIGURE 2



(1)	WAVE LENGTH	×	FREQUENCY	=	CONSTANT	
(2)	λ	×	ν	=	c	
(3)	$\frac{\text{distance}}{\text{wave}}$	×	$\frac{\text{waves}}{\text{time}}$	=	$\frac{\text{distance}}{\text{time}}$	= VELOCITY
(4)	λ (cm/wave)	×	ν (waves/sec)	=	C = (3×10^{10} cm/sec)	

Figure 3. Relationship of Wave Length and Frequency

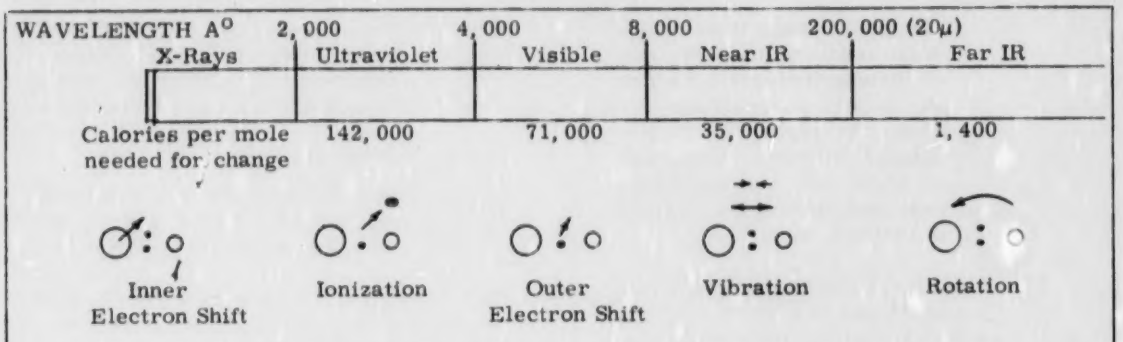


Figure 4. Electromagnetic Spectrum Showing Energy Ranges and Corresponding Electronic, Vibrational and Rotational Motions

1 Displacement of electrons is a permissible change which can occur when energy of ultraviolet and visible frequencies strikes certain atoms and molecules.

a Inner electron shift

Electrons located in the inner orbit of an atom may, when the proper frequency of radiant energy is available, shift to an orbit farther removed from the nucleus. This shift represents a change from a lower energy to a higher one. If this new position is unstable, the electron may revert to some position nearer the nucleus; the energy which was gained may then be emitted from the atom as part of its emission spectrum. The number of energy changes possible within an atom is a function of the number of electrons and the number of changes each may enter. Each possible change gives rise to a new spectral frequency. Since the frequency of radiation needed to accomplish such changes is of a high order of magnitude, the energy used is considerable in quantity.

Molecular aggregations often disintegrate in such circumstances; thus, these higher frequencies are used mainly for work with elements or very stable compounds.

b Ionization

Under a specific frequency of radiation, an electron may be physically separated from its parent atom. This process has been termed ionization. A change of energy level of this magnitude requires less energy than the inner electron shift. Such changes are characteristic of those of the rare earths, inorganic ions, transition elements and many organic compounds under frequencies within the ultraviolet range.

c Outer electron shift

The various orbital electrons in an atom may vary in the amount of energy required to shift them outwardly from the nucleus. For example, it requires less energy to shift an electron from a position more distant than it does to shift an electron outwardly from the inner orbit. Outer electron shifts occur readily in colored organic molecules for which

electronic transitions are made easier by the presence of chromophore groups which participate in resonance. Thus, the excitation of the delocalized outer electrons (pi electrons) is relatively easy and requires energy in the visible range.

2 Vibration of atoms within molecules is a permissible change which can occur when energy of near infrared frequency strikes certain organic molecules.

The atoms within a molecule are held together by attractive bonding forces. Atoms within a molecule are constantly moving toward and away from other atoms, but for purposes of theory can be said to have a certain "average" position.

The change in position of an atom in relation to another atom is called vibration. The mechanics of vibration require energy; the manner and rate of vibration of the atoms depend upon frequencies of electromagnetic radiation which strikes them. Therefore, a specific part of a molecule may absorb significant quantities of certain spectral frequencies. Such absorption will be reflected in the absorption spectrum of the compound. The energy requirements for this type of energy change are of a lower order of magnitude than those above; therefore, we would expect that the frequency required would be lower and the wave length longer. Such changes occur in organic compounds under infrared radiation.

3 Rotation of molecules is a permissible change which can occur when energy of far infrared frequency strikes certain organic molecules.

A molecule rotates around its symmetrical center. The manner and rate of rotation again depends upon the energy supplied to it.

Specific spectral frequencies of electromagnetic radiation can be employed to increase the rate of rotation. The used radiation is, in effect, absorbed and reflected in the absorption spectrum.

Organic molecules utilize infrared radiation while varying their rate and manner of rotation.

B The Lambert-Beer Law provides the basis for quantitative analysis by absorption spectroscopy. It is a combination of the Bouguer (or Bouguer-Lambert) and Beer Laws.

1 Bouguer (or Bouguer-Lambert) Law

When a beam of monochromatic radiation passes through an absorbing medium, each infinitesimally small layer of the medium decreases the intensity of the beam by a constant fraction.

Mathematically:

$$\frac{-dI}{I} = k\ db \qquad (6)$$

On integration and converting base e to base 10 logarithms,

$$\log \frac{I_o}{I} = A = Kb \qquad (7)$$

$-dI$ = increment by which incident monochromatic radiation is decreased (or absorbed) by the medium.

I = intensity of the radiation emerging from the absorbing medium.

k = proportionality constant whose value depends on the wave length and the nature of the medium; i.e., the solvent used if the absorbing medium is a solution, and the temperature.

db = increment thickness of the absorbing medium.

I_o = radiation entering the medium.

$\log \frac{I_o}{I}$ = A = absorbance (optical density)

K = 2.303 k

b = length of radiation passing through the medium (i.e., the width of the cell, generally express in cm.)

2 Beer's Law

Each molecule of an absorbing medium absorbs the same fraction of radiation incident upon it regardless of concentration.

Mathematically:

$$\frac{-dI}{I} = k' \, dc \qquad (8)$$

On integration and converting base e to base 10 logarithms,

$$\log \frac{I_o}{I} = K' c \qquad (9)$$

k' = a proportionality constant whose value is governed by the same factors which determine the value of k.

dc = increment concentration of the absorbing medium.

K' = 2.303 k'

c = concentration of the absorbing medium (in the case of a solution c is generally expressed in moles/liter.)

3 Lambert-Beer Law

$$A = \log \frac{I_o}{D} = e \, b \, c \qquad (10)$$

e = a constant obtained by combining K plus K'. When b is expressed in cm and c in moles/liter, e is called the molar absorptivity.

4 The term transmittance is sometimes used to express how much radiation has been absorbed by a medium.

$$\text{Transmittance (T)} = \frac{I}{I_o} \qquad (11)$$

$$\text{\% Transmittance (\%T)} = \frac{I}{I_o} 100 \qquad (12)$$

The relationship between absorbance and transmittance is given by the expression:

$$A = \log \frac{I}{T}$$

5 The application of the Lambert-Beer Law to a problem involving quantitative analysis is made by the use of a calibration curve (or graph). See Figure 5.

Several standard solutions containing known concentrations of the material under analysis are "read" in the spectrophotometer. Figure 5 is prepared by graphing concentrations vs. corresponding absorbance readings.

If a straight line is obtained, the material is said to follow Beer's Law in the concentration range involved. The absorbance of the sample is then "read" and the corresponding concentration obtained from the calibration curve.

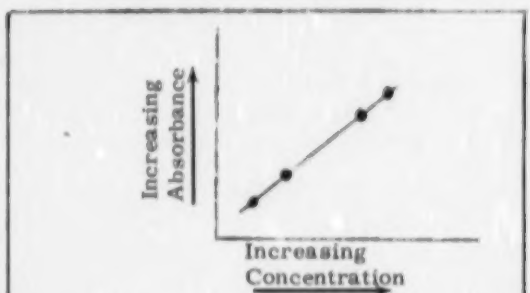


Figure 5.

ACKNOWLEDGMENT:

This outline contains certain portions from a previous outline by Betty Ann Punghorst, former Chemist, National Training Center.

RANGE	SOURCE OF RADIANT ENERGY	ABSORPTION BY SAMPLE		DETECTION OF RADIANT ENERGY TRANSMITTED
		CHEMICAL NATURE OF SAMPLE	TYPE OF SAMPLE CELL USED	
Ultraviolet	Hydrogen Arc	Inorganic ions and Organic Molecules	Quartz Fluorite	Photoelectric Cells Photographic Plates
Visible	Incandescent Tungsten Bulb	Colored Inorganic and Organic Molecules	Glass	Eye Photographic Plates Photoelectric Cells
Infrared	Nernst Glower Globar Lamp	Organic Molecules	Sodium Chloride or Potassium Bromide	Thermocouple

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This outline was prepared by C. R. Feldmann, National Training Center, MOTD, OWPO, USEPA, Cincinnati, Ohio 45268.

Descriptors: Chemical Analysis, Water Tests, Spectroscopy, Spectrophotometry

FLAME PHOTOMETRY

I PRELIMINARY

Flame photometry is the art and science of applying thermal energy (heat) to elements in order to effect orbital shifts which produce measurable characteristic radiations. The color of the emission and the intensity of brightness of emission permit both qualitative and quantitative identification.

The application of a very hot flame (2000° C or more) produces excitation of the element, caused by the raising of an electron to a higher energy level and is followed by the loss of a small amount of energy in the form of radiant energy as the electron falls back into its original position or to a lower energy level.

II INSTRUMENTATION

The six essential parts of a flame photometer are: pressure regulators and flow meters for the fuel gases, atomizer, burner, optical system, photosensitive detector and an instrument for indicating or recording output of the detector. These components are schematically shown in Figure 1.

A Atomizer and Burner

Numerous variations in atomizer and burner designs have been used. Figure 2 depicts the integral aspirator-burner used in Beckman instruments. The sample is introduced through the innermost concentric tube, a vertical

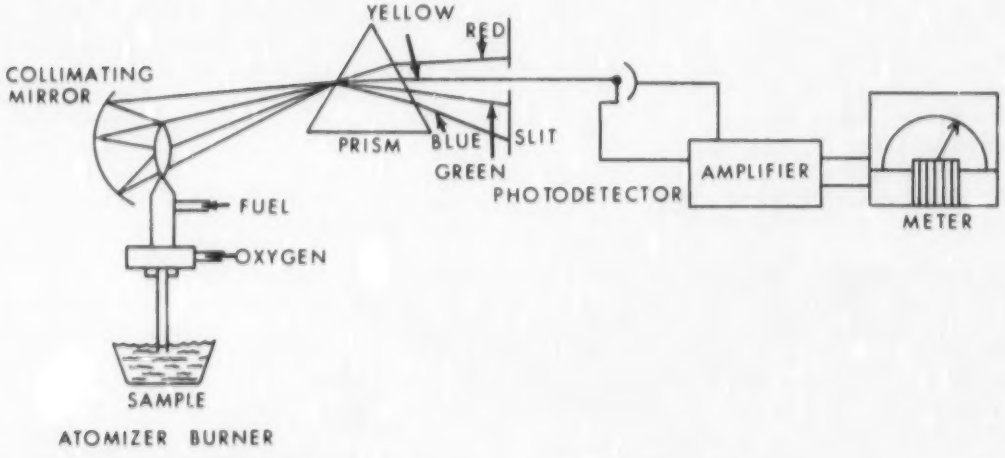


FIGURE 1. SIMPLIFIED DIAGRAM OF A FLAME PHOTOMETER

palladium capillary. A concentric channel provides oxygen, and its tip is constricted to form an orifice. Oxygen is passed from this orifice causing the sample solution to be drawn up to the tip of the inner capillary. There, the liquid is sheared off and dispersed into droplets. All droplets are introduced directly into flame, with a sample consumption of 1 - 2 ml per minute.

The main requirement of the burner is production of a steady flame when supplied with fuel and oxygen or air at constant pressures. In the Beckman aspirator-burner, a concentric channel provides oxygen to operate the atomizer and the flame. The additional concentric channel provides fuel for the flame.

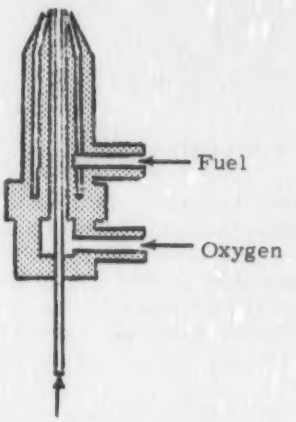


Figure 2. DETAILED DIAGRAM OF BURNER-ATOMIZER

B Optical System, Photosensitive Detector and Amplifier

The optical system must collect the light from the steadiest part of the flame, render it monochromatic with a prism, grating or filters, and then focus it onto the photosensitive surface of the detector. Use of filter photometers is least desirable due to their limited resolution. Flame spectrophotometers improve application as they will separate emissions in a mixture of metals, such as manganese lines at 403.3 nm and the potassium lines at 404.6 nm Placement of a concave mirror behind the flame so that the flame is at the center of the curvature increases intensity of flame emission by a factor of 2.

Any photosensitive device may be used in a flame photometer. The detector must have a response in the portion of the spectrum to be used and have good sensitivity. The photomultiplier tube is the preferred detector for flame spectrophotometers.

The amplifier increases the signal from the phototube and improves resolution between close spectral lines. It also permits identification of elements present in samples when the concentration is very small.

III APPLICATIONS OF FLAME PHOTOMETRY TO WATER ANALYSES

Measurement of sodium and potassium in the past has been confined to complex, tedious and time-consuming gravimetric procedures. The flame technique enables the analyst to perform these determinations in a matter of seconds. If these metals alone were the only elements capable of measurement by flame photometry the use of the instrument could still be justified in a great many laboratories.

Other cations which may be detected and measured in waters and waste materials are calcium, magnesium, lithium, copper, and others. Table 1 includes those elements which may be measured with commercially available equipment, including ultra-violet and photomultiplier accessories.

Table 1 does not include wavebands which occur in the infrared spectrum. Sodium, for example, has an emission band at 819 nm which is not detectable with the common instruments.

Many other metals, including the rare earths, can be measured using the flame technique but they are not included in the table because

Table 1

	Wavelength	Approximate Sensitivity mg/l		Wavelength	Approximate Sensitivity mg/l
Aluminum	484.2	2	Lead	405?	2
	467.2	3		368?	2
	396.2	4		364?	3
Barium	553.6	0.3	Lithium	670.8	0.002
	493	0.4			
			Magnesium	371?	0.1
Beryllium	471	25		383?	0.1
	510	100		285.2	0.2
Boron	548	1	Manganese	403	0.01
	521	2		279*	1
	495	3		561	2
Cadmium	326.1?	2	Mercury	235.7*	10
	228.8*	40			
			Potassium	766.5	0.001
Calcium	422.7	0.003		404.6?	0.2
	622	0.004		344.7?	3
	554	0.01			
			Silver	338.3?	0.05
Chromium	425.4	0.1		328.1?	0.1
	360?	0.1			
	520	0.1	Sodium	589.3?	0.002
				330.3?	1
Copper	324?	0.01			
	327?	0.01	Strontium	460.7	0.02
				681	0.01
Iron	372	0.2		407.8	0.5
	386	0.2			
	373	0.3	Zinc	213.9*	500
				500	200

* = Ultraviolet spectrum

? = Doubtful detection in visible spectrum

the necessity for their measurement in water is a rare occurrence.

IV INTERFERENCES

A Spectroscopic Interferences

Energy at other wave lengths or from other elements than those intended to be measured may reach the detector. This problem is related to the resolution of the instrument and slit widths used.

Many of the instrumental difficulties are related to reproducibility of the flame. The quality and composition of the fuel affect the constancy and temperature of the flame which in turn influences the energy of emission. Likewise, slight variations in fuel pressures and ratios affect the reproducibility of the flame with reference to shape, temperature, background, rate of sample consumption, etc. In some cases, the temperature of the flame is the limiting factor in determining the presence of a metal. (The alkaline earth metals emit radiations at "low" temperatures, whereas other metals require very "hot" flames.)

Table 2 indicates temperatures obtainable with different fuel-oxidant mixtures.

Table 2.
Approximate Temperatures of Fuel-Oxidant Mixtures for Flame Photometer Use

Fuel-Oxidant	Approximate Temp. °C
Hydrogen - air	2100
Hydrogen - oxygen	2700 - 2800
Acetylene - oxygen	3100
Acetylene - air *	2000 - 2200
Propane - oxygen	2700 - 2800
Illuminating gas - oxygen	2800
Cyanogen - oxygen **	4900

* Undesirable because of carbon deposits.
** Used in research problems.

Emission reading of spectral lines always includes any contribution from the flame background emission on which the line is superimposed. When the photometer includes a monochromator, it is possible to read the background radiation in the presence of the test element. First, the line + background intensity is measured in the normal manner at the peak or crest of the band system. Next, the wave length dial is rotated slowly until emission readings decrease to a minimum at a wave length located off to one side or the other of the emission line or band. It is usually preferable to read the background at a lower wave length than the peak. Background reading is subtracted from the line + background reading.

Products of combustion may affect the characteristics of the flame or may affect the optical system by fogging or coating of lenses and mirrors.

B Factors Related to the Composition of the Sample

An element may be self-absorbing -- a phenomenon in which the energy of excitation is not proportional to the concentration of the element. As previously discussed, exictation is followed by loss of energy in the form of radiation as the electron falls back to its original position or to a lower energy level. During passage of radiant energy through the outer fringes of the flame, this energy is subject to absorption through collision with atoms of its own kind present in the ground energy level. Absorption of radiant energy weakens the strength of the spectrum line. Using the emission line at 589 nm for sodium, Figure 3 indicates that the line ceases to be linear at 13 mg/l. As the sodium concentration increases, the self-absorption effects become more pronounced. Sample dilution to permit reading on linear portion of the curve is often practiced.

Two or more elements present in the sample may produce radiant energy at

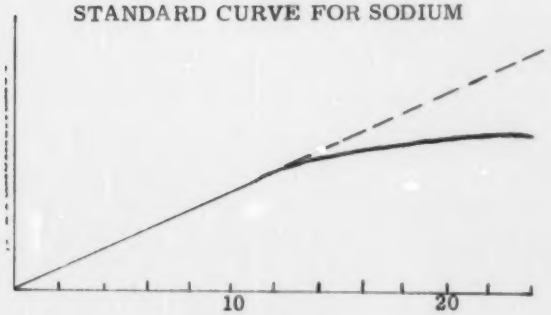
the same, or near the same wavelength. For instance, calcium at 423 nm and chromium at 425 nm could interfere with each other by additive effect. The correction may be to dilute out the unwanted metal or measure one of the emissions at a different wavelength.

The emission energy of one element may be enhanced or depressed by energies from other elements. This phenomenon (radiation interference) occurs when one element causes another to modify its actual emission intensity in either a negative or positive manner. Correction is obtained by dilution or by controlled interference addition.

Other types of difficulties encountered are too numerous to list here. In general, they may be overcome by improved instruments (high resolution, narrower slit openings, optics, flame adjustment) or possibly by special techniques.

Some inexpensive instruments, designed for limited use, may employ illuminating gas with air or propane with air as a matter of economy or convenience.

STANDARD CURVE FOR SODIUM



mg Sodium/l

Figure 3

V TECHNIQUES

The following techniques are intended to serve as examples of current procedures in use for routine samples and for special samples where corrective procedures are indicated.

A Emission Intensity vs. Concentration

This is the classical procedure in flame photometry. Solutions (standards) containing known concentrations of test elements are compared with an unknown sample. This technique is applicable only when no interference is present.

B Radiation Buffers

For measurements of alkaline earth metals (sodium, potassium, calcium, magnesium) radiation buffers are prepared as solutions saturated with regard to each metal, respectively. A potassium buffer, for example, is prepared by saturating distilled water with sodium, calcium, and magnesium chloride. A calcium buffer in turn is saturated with sodium, potassium and magnesium chloride.

C Preparation of Radiation Buffers

For a sodium measurement, the buffer solution is added equally to samples and standards so that the interferences are alike for all readings, thereby cancelling each other (see Table 3).

D Instrument Improvement

Potassium emits energy bands at 766, 405, and 345 nm. The bands are at opposite ends of the spectrum and the 405 and 345 bands are not usable in the visible spectrum. The 766 line also loses sensitivity because of its proximity to the infrared region. Use of a red sensitive phototube or photomultiplier, however, permits measurement with an ordinary instrument at concentrations as low as 0.1 mg/l, or less. This approach is applicable to other elements also.

E Standard Addition

Equal volumes of the sample are added to a series of standard solutions containing different known quantities of test element, all diluted to the same volume (see Table 4). Emission intensities of the resulting solutions are then determined at the wavelength of maximum emission and at a suitable point on the flame background. After subtracting the background emission, the resulting net emissions are plotted linearly against the concentration of the increments of the standard solutions that were mixed with the unknown. The percent transmission of the mixture containing unknown sample and zero standard (distilled water) is doubled and the concentration corresponding to this point on the graph will be the concentration of the undiluted unknown sample. This can be explained algebraically in conjunction with Figure 4.

F Internal-Standard Method

The method consists of adding to each sample and standard a fixed quantity of internal standard element. The element must be one not already present in the sample. Lithium is usually the internal standard used. This method is most convenient when using instruments having dual detectors. The emission intensities of standards and samples are read simultaneously or successively depending upon instrumentation.

G Separation of Interferences

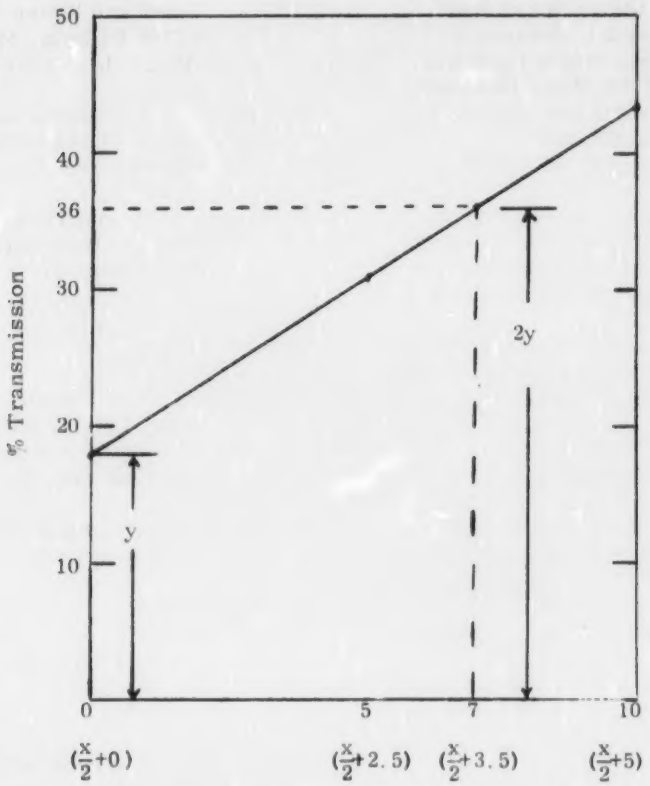
In cases where certain elements interfere, they may be physically removed, or the interference may be "blocked out" by reading the emission at different wavelengths. To measure lithium, for example, calcium, barium, and strontium are precipitated as carbonates of the metals. The lithium is retained in the filtrate and measured at a wavelength of 671 nm.

	NaCl	KCl	$CaCl_2$	$MgCl_2$
Sodium Buffer	-	+	+	+
Potassium Buffer	+	-	+	+
Calcium Buffer	+	+	-	+
Magnesium Buffer	+	+	+	-

Table 3

Conc. of standards	0.0 mg/l	5.0 mg/l	10.0 mg/l
Volume of standard added to sample	10.0 ml	10.0 ml	10.0 ml
Volume of sample used	10.0 ml	10.0 ml	10.0 ml
Concentration of element in each portion of mixture	$\frac{x}{2}$ + 0 mg/l	$\frac{x}{2}$ + 2.5 mg/l	$\frac{x}{2}$ + 5 mg/l

Table 4



Let x = concentration of element in unknown sample.

Then Y = % transmission of an equal mixture of unknown sample and zero standard, or

$$Y = \frac{x}{2} + \frac{0}{2}$$ which simplifies to $2Y = x$

$\therefore$ $2Y = \frac{x}{2} + 3.5$ (from the example in Figure 4)

by substitution, $x = \frac{x}{2} + 3.5$

$$\frac{x}{2} = 3.5$$

$$x = 7 \text{ mg/l}$$

Figure 4

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Descriptors: Chemical Analysis, Water Tests, Flame Photometry, Spectrophotometry, Spectroscopy

DETERMINATION OF CALCIUM AND MAGNESIUM HARDNESS

I INTRODUCTION

A Definition of Hardness

USPHS - "In natural waters, hardness is a characteristic of water which represents the total concentration of just the calcium and magnesium ions expressed as calcium carbonate. If present in significant amounts, other hardness-producing metallic ions should be included."

B Other Definitions in Use

1 Some confusion exists in understanding the concept of hardness as a result of several definitions presently used.

2 Soap hardness definition includes hydrogen ion because it has the capacity to precipitate soap. Present definition excludes hydrogen ion because it is not considered metallic.

3 Other agencies define hardness as "the property attributable to presence of alkaline-earths".

4 USPHS definition is best in relation to objections of hardness in water.

II CAUSES OF HARDNESS IN WATERS OF VARIOUS REGIONS OF THE U. S.

A Hardness will vary throughout the country depending on:

1 Leaching action of water traversing over and through various types of geological formations.

2 Discharge of industrial and domestic wastes to water courses.

3 Uses of water which result in change in hardness, such as irrigation and water softening process.

B Objections to Hardness

1 Soap-destroying properties

2 Scale formation

C Removal and Control

Hardness may be removed and controlled through the use of various softening operations such as zeolite, lime-soda, and hot phosphate processes. It can also be removed by simple distillation or complex formation with surface active agents (detergents).

III DETERMINATION OF HARDNESS

A Two Methods in Use[6]

1 Complexiметric method (EDTA)

2 Calculation - by the use of appropriate factors, the hardness due to ions other than calcium and magnesium may be converted to an equivalent calcium carbonate hardness.

B Complexiметric Method

1 Principle of determination

Ethylenediaminetetra acetic acid (EDTA) is a sparingly soluble amino polycarboxylic acid which forms slightly ionized and very stable colorless complexes with the alkaline-earth metals.

2 Interferences: iron, manganese, nickel, and zinc.

3 Procedure: Time and pH considerations.

4 Calculations of total hardness assuming a known volume of titrant of EDTA.

5 Precision and accuracy.

C Determination of Calcium Hardness

1 Principle of determinations

Murexide indicator forms a salmon-colored complex with calcium whose ionization constant is of a higher value than that of the Ca EDTA complex.

2 Interferences: Heavy metals and Sr.

3 Procedure: Time of tritation and proper lighting conditions are critical factors.

4 Calculation of Ca hardness.

5 Precision and accuracy.

D Determination of Magnesium Hardness

1 Calculation by difference method most commonly used.

2 Equivalent of Ca hardness is subtracted from total hardness equivalents, the difference attributable to magnesium equivalents.

3 Other methods such as pyrophosphate method, where calculation by difference method cannot be used.

IV ANALYTICAL QUALITY CONTROL METHODS

A The Environmental Protection Agency, Analytical Quality Control Laboratory has published a manual titled Methods for Chemical Analysis of Water and Wastes, 1974.

B The procedure for the determination of hardness, as discussed in this manual, was excerpted from the 13th ed. of Standard Methods[4] and part 23 of ASTM.[5]

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Descriptors: Calcium, Chemical Analysis, Hardness, Magnesium, Water Analysis, Calcium Carbonate, Calcium Compounds, Magnesium Carbonate

FLAMELESS MERCURY FOR ANALYTICAL METHODS FOR TRACE METALS

DETERMINATION OF MERCURY

I INTRODUCTION

There are many forms of mercury, some more toxic to humans than others. Although metallic mercury and its inorganic, alkoxyalkyl, and aryl compounds can have detrimental effects on man and other animals, it has become clear that methylmercury poses a particularly serious problem. It appears that mercury enters the food chain as methyl mercury after conversion by microorganisms in the silt of waterways.

Sources of mercury in industrial and agricultural countries fall into the following categories: 1) chlor-alkali plants, 2) industrial processes involving the use of mercurial catalysts, 3) slimicides, used primarily in the paper-pulp industry, 4) seed treatment, 5) burning of fossil fuels, 6) natural occurence from geological formations, and 7) miscellaneous sources.

Early in 1970 fish in Lake St. Clair above Detroit were shown to contain hazardous levels of methyl mercury. However, even before this other countries such as Japan were having serious problems with mercury poisoning. "Minamata Disease" or methyl mercury poisoning due to ingestion of contaminated fish occurred in a village near the Minamata Bay, Japan, from 1953 through the 1960's, and affected at least 121 children and adults. Consequently, the finding of high levels of methyl mercury in Lake St. Clair caused the United States and Canada to ban fishing in the lake.

A study was carried out by the Office of Water Supply during 1971 analyzing 698 samples of raw and finished waters collected from 273 communities. Of these 273 communities, 261 showed no detectable quantities or concentration of less than 0.001 ppm. In eleven of the communities the mercury concentration ranged from 0.0010 to 0.0048 ppm.

After the discovery of mercury contamination in fish, the importance of the mercury content of waters can be seen by the decreasing allowable limits. The 1962 edition of the Public Health Service Drinking Water Standards did not list a limit for mercury. However, in 1970 a tentative standard of 0.005 mg/l limit was proposed. Recently, March 1975, the Interim Primary Drinking Water Standards proposed a limit of 0.002 mg/l.

II METHODS

A Dithizone

Until about 1964 the method of choice for analysis of mercury was the dithizone method. This method utilized a colorimetric determination of the dithizone complex with mercury. The method has been characterized as relatively insensitive and requiring excessive amounts of sample when levels of mercury are low. The analyst must have experience in order to obtain meaningful results due to the possibility of loss of volatile forms of mercury during a hot acid digestion procedure. The method covered the range of 0.005 mg/l to .035 mg/l.

B Emission Spectroscopy

The emission spectrophotometric determination of mercury was also carried out. However, the cost of the instrument made this method considerably more expensive than the dithizone method. The detection limit fell in the range of about 5 mg/l so no increase in sensitivity could be obtained.

C Atomic Absorption

The detection limit by direct aspiration of a sample into the instrument was claimed to be 0.5 mg/l. However, in actual practice the limit was closer to 5.0 mg/l. A concentration step before aspiration by

chelation with ammonium pyrrolidine dithiocarbamate and extraction with methyl isobutyl ketone, reduced the detection limit to about 0.2 mg/l. Additional sensitivity was claimed by using the sample boat which evaporated one milliliter of sample in a boat like device followed by ignition of boat in the flame. This helped reduce the detection limit to around 0.02 mg/l but here again in actual practice the sensitivity was probably less.

D Gas Chromatography

A swedish method utilized an electron capture detector to detect materials at a sensitivity approaching 0.001 mg/l in favorable cases. This procedure was good for the organic forms of mercury contamination such as methyl mercury, ethyl mercury and methoxy ethyl mercury, and phenyl mercury. Dimethyl mercury and the inorganic forms of mercury gave no response in this procedure.

E Flameless Atomic Absorption

It had long been known that the metallic mercury vapor absorbed energy at 2537 Å. However, it was not until 1968 that a method was practical. This method converts all forms of mercury present in the sample to the metallic form. Therefore, the results in this method are only for total mercury since there is no differentiation. The detection limit for mercury was lowered to a point that made adoption of low standards analytically practicable. The detection limit for mercury by the flameless method was reduced to 0.0002 mg/l.

This procedure has become the standard analytical procedure for the analysis of mercury. Both the National Pollution Discharge Elimination System's analytical methods and the methods recommended to meet the Primary Drinking Water Standards recommend the flameless atomic absorption technique.

III FLAMELESS METHOD

A Chemistry

The procedure covered here is the procedure recommended in the Environmental Protection Agency's manual of "Methods for Chemical Analysis of Water and Wastes." The method is applicable to drinking, surface, and saline waters, domestic and industrial wastes.

In addition to inorganic forms of mercury, organic mercurials may also be present in a sample. These organo-mercury compounds will not respond to the falmeless atomic absorption technique unless they are first broken down and converted to mercuric ions. Potassium permanganate oxidizes many of these compounds, but recent studies have shown that a number of organic mercury compounds, including phenyl mercuric acetate and methyl mercuric chloride, are only partially oxidized by this reagent. Potassium persulfate has been found to give approximately 100% recovery when used as the oxidant with these compounds. Therefore, a persulfate oxidation step following the addition of the potassium permanganate has been included to insure that organo-mercury compounds, if present, will be oxidized to the mercuric ion before measurement. A heat step is required for methyl mercuric chloride when present in or spiked to a natural system. The range of the method may be varied through instrument and/or recorder expansion. Using a 100 ml sample, a detection limit of 0.2 μg Hg/l can be achieved; concentrations below this level should be reported as < 0.2.

Possible interference from sulfide is eliminated by the addition of potassium permanganate. Concentrations as high as 20 mg/l of sulfide as sodium sulfide do not interfere with the recovery of added inorganic mercury from distilled water. Copper has also been reported to interfere; however, copper concentrations as high as 10 mg/l had no effect on recovery of mercury from

spiked samples. Sea waters, brines and industrial effluents high in chlorides require additional permanganate (as much as 25 ml). During the oxidation step chlorides are converted to free chlorine which will also absorb energy at 253 nm. Care must be taken to assure that the free chlorine is absent before the mercury is reduced and swept into the cell. This may be accomplished by using an excess of the hydroxylamine sulfate reagent (25 ml). In addition, the dead air space in the aeration bottle must be purged before the addition of stannous sulfate. Both inorganic and organic mercury spikes have been quantitatively recovered from sea water using this technique.

Interference from certain volatile organic materials which will absorb at this wavelength (253 nm) is also possible. A preliminary run without reagents should determine if this type of interference is present. If an interference is found to be present, the sample should be analyzed both by using the regular procedure and again under oxidizing conditions only, that is without the reducing reagents. The true mercury value can then be obtained by subtracting the two values.

The chemical procedure involves obtaining a sample of at least 100 ml. Until more conclusive data are obtained, preservation of samples can be accomplished by acidification with nitric acid to a pH of 2 or lower immediately at the time of collection. The 100 ml sample is placed in a 300 ml BOD bottle. Add 5 ml of concentrated sulfuric acid and 2.5 ml of concentrated nitric acid, mixing after each addition. Add 15 ml of potassium permanganate solution (5% solution) to each bottle. For sewage samples additional potassium permanganate may be required. Shake and add additional amounts of potassium permanganate, if necessary, until the purple color exists for at least 15 minutes. Add 8 ml of potassium persulfate (5% solution) to each bottle and heat for two hours in a water bath at 95°C. Cool and add 6 ml of sodium chloride-hydroxylamine sulfate (12 grams of each diluted to 100 ml) to reduce the excess potassium permanganate. Allow to stand at least 30 seconds.

Up to this point all samples and standards being run can be treated in a group. However, the final step should be done just before the BOD bottle containing the solution is attached to the instrument. This is to reduce the possibility of loss of any mercury vapor. The final step in the procedure is to add 5 ml of stannous sulfate (25 g diluted to 250 ml with 0.5 N sulfuric acid). After the BOD bottle has been attached the sample is allowed to stand quietly without manual agitation. The circulating pump is allowed to run continuously. The absorbance will increase and reach maximum within one minute. As soon as the indicating device (meter or recorder) levels off the reading is taken and the mercury vapor trapped.

B Aeration Gas Flow Path

Once the mercury is reduced to metallic mercury by the stannous sulfate, the metallic vapor begins to escape from the solution. In order to quantitatively drive off all the vapor a pump is used to push air into the solution through an aeration device such as a glass frit of coarse porosity. The air acts as a carrier gas for the vapor. An aeration device may be constructed as shown in Figure 1.

Any peristaltic pump capable of delivering one liter of air per minute may be used. The pump should be checked occasionally via a rotometer to assure that sufficient flow is being provided.

The flow path of the procedure can be set up in two ways, in an open mode and a closed mode. The closed mode recirculates the mercury vapor through the entire flow path, including the absorption cell, until a manual valve shunts the vapors to a trap. The open mode allows the vapors to pass only one time through the absorption tube and from there it goes to a trap.

There are several pieces of equipment involved in the flow path that are common to both modes. The aeration bottle has been mentioned before, next in line should come a desiccant (of magnesium perchlorate) to adsorb water vapors in order to prevent these from condensing in the absorption tube. If a conventional atomic absorption

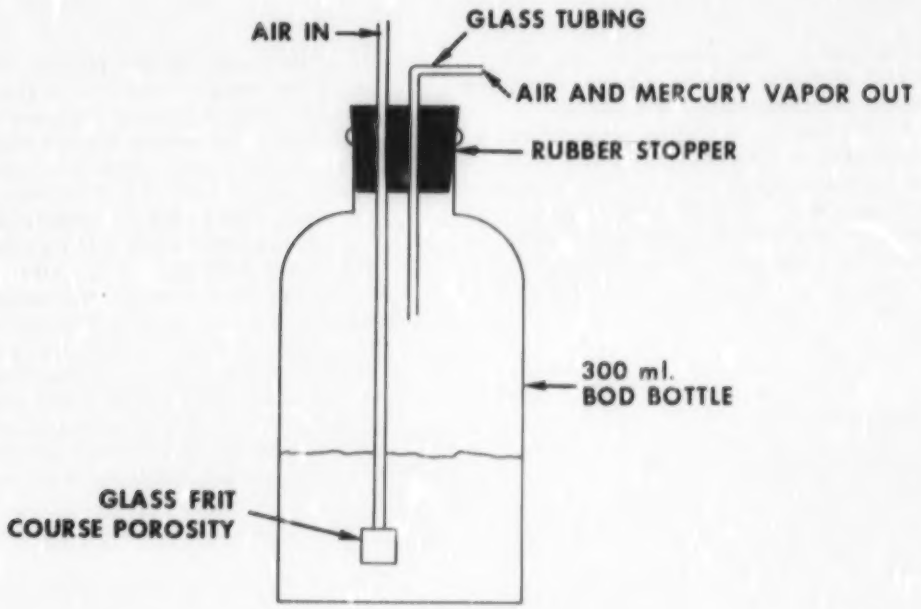


Figure 1. Aeration Bottle

spectrophotometer is being used, the desiccant can be replaced with a small 60 watt lamp. This is positioned to shine on the tube itself to raise the temperature inside the tube thus preventing condensation. Next in the flow path after the desiccant would come the absorption cell, or instrument.

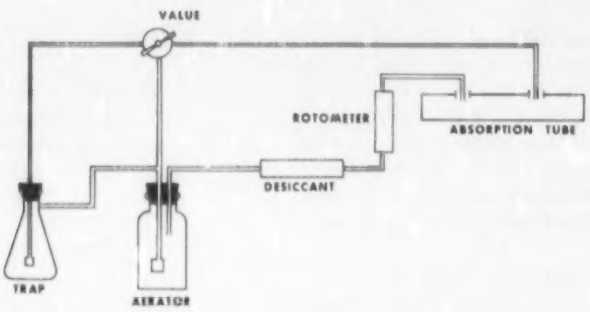
In the open mode a trap for the mercury vapors would follow the absorption tube. In the closed mode a valve would follow. The position of each of these pieces can be seen in Figure 2.

The absorption tube or cell can be a standard spectrophotometer cell that is 10 cm long and having quartz end windows. Suitable cells may be constructed from plexiglass tubing 1 inch outside diameter and $4\frac{1}{2}$ inches long. The ends are ground perpendicular to the longitudinal axis and quartz windows 1 inch in diameter and one sixteenth of an inch thick are cemented in place. Gas inlet and outlet ports (also of plexiglass but $\frac{1}{4}$ inch outside diameter) are attached approximately $\frac{1}{2}$ inch from each end.

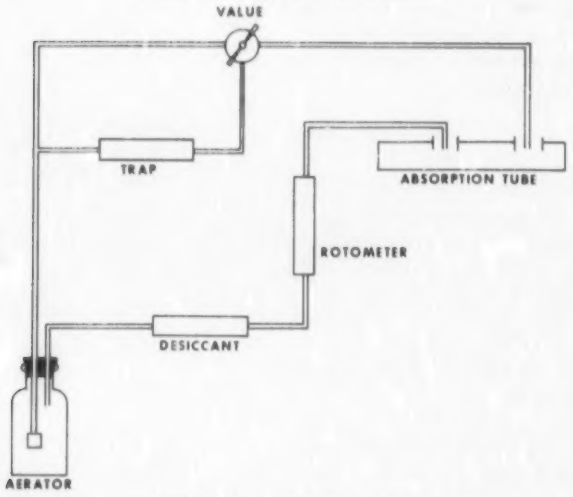
C Instrumentation

Any atomic absorption spectrophotometer having an open sample presentation area in which the absorption tube can be mounted is suitable. The absorption tube is strapped to a burner for support and aligned in the beam by use of two 2 x 2 cards. One inch diameter holes are cut in the center of each card; the cards are placed over each end of the cell. The cell is then positioned and adjusted vertically and horizontally to give the maximum transmittance.

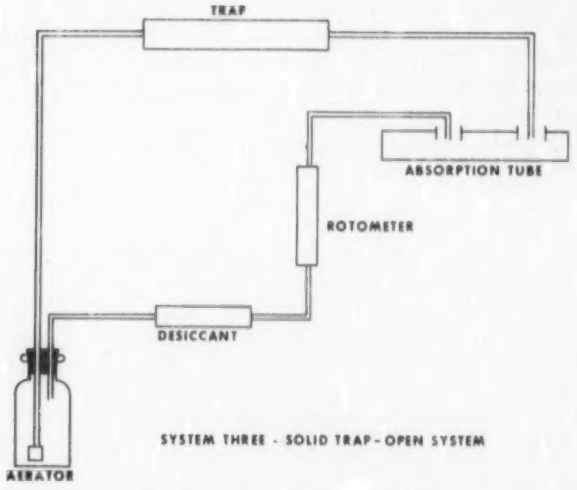
There are available on the market instruments designed specifically for the determination of mercury by the flameless atomic absorption method. Usually they are complete and contain the absorption tube and pump inside the instrument. The main advantage of these instruments is that they are considerably cheaper than an atomic absorption instrument. However, their chief disadvantage lies in the fact that they can be used only for mercury while an atomic absorption instrument with some additional equipment (lamps) can be used for about 40 metals.



SYSTEM ONE - LIQUID TRAP CLOSED SYSTEM



SYSTEM TWO - SOLID TRAP CLOSED SYSTEM



SYSTEM THREE - SOLID TRAP - OPEN SYSTEM

Figure 3. Flow Systems

There is also available an automated method which utilized the Technicon Auto Analyzer. This method is described in detail in the EPA Methods Manual. The method is applicable to surface waters and may be applicable to saline water, wastewater effluents and domestic sewage providing potential interferences are not present.

Regardless of what instrument is used, its calibration should be checked originally upon receipt and standards run each time samples are to be run in order to verify the calibration. The standards are treated in the same method except that if no organic mercury is used as the standard, the heating step can be omitted.

IV SUMMARY

The determination of the mercury content of waters has become a necessary analysis for the health of the consuming public. The method of choice has become the flameless atomic absorption procedure. Besides being simple to perform it is sensitive enough to determine the limit set for the permissible content of mercury in water.

The method can be carried out on any atomic absorption instrument that has enough physical space in its burner compartment in which to install the absorption cell. However, there are available on the market, instruments designed specifically to determine mercury via the flameless method. These instruments are generally considerably less expensive than a conventional atomic absorption spectrophotometer but have the drawback of being able to be used for only that determination.

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Descriptors: Heavy Metals, Mercury, Water Pollution, Chemical Analysis, Metals, Spectroscopy, Spectrophotometers

DETERMINATION OF LEAD

I INTRODUCTION

Lead (Pb) is a serious cumulative body poison; it is well known for its toxicity in both acute and chronic exposures. In technologically developed countries the widespread use of lead multiplies the risk of exposure of the population to excessive levels. For this reason, constant surveillance of the lead exposure of the general population via food, air and water is necessary.

The presence of lead in water may arise from industrial, mine and smelter discharges, or from the dissolution of old lead plumbing. Tap waters which are soft, acid, and not suitably treated may contain lead resulting from an attack on the lead service pipes. Lake and river waters of the United States usually contain less than 0.05 mg/l of lead, although concentrations in excess of this have been reported. Young children present a special case in lead intoxication both in terms of tolerated intake and the severity of the symptoms. The most prevalent source of lead poisoning of children up to three years of age has been lead-containing paint still found in some older homes.

Because of the toxicity of lead to humans and because there is little information on the effectiveness of treatment processes in decreasing lead concentrations, it has been recommended that 0.05 mg/l of lead not be exceeded in public water supply sources. This number then would tend to set the limit for any analytical method which might be under consideration for use in analyzing for lead.

II METHODS

The methods used to analyze for lead are, in general, the same as those of any other heavy metal. However, there is no method for lead similar to the flameless method for mercury. The method recommended by the USEPA Methods manual is an atomic absorption method utilizing a concentration of the lead content by a chelating-extraction procedure. Other methods are available for those who are not bound to use the USEPA method.

A Dithizone

This method has been used for many years for the determination of many of the heavy metals including lead. Dithizone dissolved in carbon tetrachloride will extract lead from a slightly basic (8.5 - 9.0) solution. The lead and dithizone form a metal complex, lead dithizonate, which is soluable in carbon tetrachloride, with the formation of a red color. Measurement of the amount of red color formed yields an estimation of the lead present.

The method has sufficient sensitivity to meet the standard limit of 0.05 mg/l. Standard Methods gives the approximate minimum detection limit in water as 2 μg of Pb. The main drawback of the method is in the many operations the analyst must perform. The precision and accuracy of the method can suffer greatly due to the analyst's handling of the various operations. Analysts with long experience with the method have been able to produce acceptable results.

The procedure for the dithizone method for normal drinking waters, low in organic matter and tin, is brief and adequate. However, for industrial wastes and waters containing high organic concentrations a pretreatment step must be added. This additional step is a digestion procedure, either with a mixture of nitric and sulfuric acids or, when the organic matter is difficult to oxidize, with nitric and perchloric acids. This procedure can introduce even more error in loss of the metals during heating to dryness and is even hazardous if not followed closely.

B Other Instrumental Methods

There are other instrumental methods available even when atomic absorption is excluded. These methods would include

polarography, emission spectroscopy, neutron activation and x-ray fluorescence. Each has its own strong and weak points. Most are expensive to the point of exclusion in most laboratories but can be used to determine the concentration of lead in a sample.

C Atomic Absorption

Most metals, including lead, may be readily determined by atomic absorption spectroscopy. The method is usually simple, rapid and applicable to a large number of metals in drinking, surface and saline waters, and domestic and industrial wastes. While drinking waters may be analyzed directly, domestic and industrial wastes require processing to solubilize suspended material. Sludges and sediments and other solid type samples may also be analyzed after proper pretreatment.

Detection limits, sensitivity and optimum ranges of the metals will vary with the various makes and models of satisfactory atomic absorption spectrophotometers. The data shown in Table 1, however, provide some indication of the actual concentration ranges measurable with conventional atomization. In the majority of instances the concentration range shown in the table may be extended much lower with scale expansion and conversely extended upwards by using a less sensitive wavelength or by rotating the burner 90 degrees. Detection limits may also be extended through concentration of the sample, through solvent extraction techniques and/or the use of the so called furnace techniques. The latter includes the heated graphite atomizer, the carbon rod and the tantalum strip accessories. When using furnace techniques, however, the analyst should be cautioned as to possible chemical reactions occurring at elevated temperatures which may result in either suppression or enhancement of the analysis element. Methods of standard addition are mandatory with these furnace techniques to insure valid data.

For levels of lead below 100 μg/l, an extraction procedure is recommended. This extraction procedure is carried out at a pH of 2.8 which is the optimum pH for the extraction of lead. However, if many of the metals are to be analyzed in the same sample, either larger sample volumes must be extracted or individual extractions made for each metal being determined.

III EXTRACTION PROCEDURE

Extraction procedure with pyrrolidine dithiocarbamic acid (PDCA) in chloroform.

A Transfer 200 ml of sample into a 250 ml separatory funnel, add 2 drops bromphenol blue indicator solution and mix.

B Prepare a blank and sufficient standards in the same manner and adjust the volume of each to approximately 200 ml with deionized distilled water. All of the metals to be determined may be combined into single solutions at the appropriate concentration levels.

C Adjust the pH by addition of 2N NH_4OH solution until a blue color persists. Add HCl dropwise until the blue color just disappears; then add 2.0 ml HCl in excess. The pH at this point should be 2.3. (The pH adjustment may be made with a pH meter instead of using indicator.)

D Add 5 ml of PDCA-chloroform reagent and shake vigorously for 2 minutes. Allow the phases to separate and drain the chloroform layer into a 100 ml beaker.

E Add a second portion of 5 ml PDCA-chloroform reagent and shake vigorously for 2 minutes. Allow the phases to separate and combine the chloroform phase with that obtained in step (D).

F Determine the pH of the aqueous phase and adjust to 4.5.

G Repeat step (D) again combining the solvent extracts.

H Readjust the pH to 5.5, extract, readjust to 6.5 and extract a fifth time. Combine all extracts and evaporate to dryness on a steam bath.

TABLE I
Atomic Absorption Concentration Ranges With Conventional Atomization***

Metal	Detection Limit mg/l	Sensitivity mg/l	Optimum Concentration Range mg/l
Aluminum	0.1	1	5 – 100
Antimony	0.2	0.5	1 – 40
Arsenic*	0.002	–	0.002 – 0.02
Barium	0.03	0.4	1 – 20
Beryllium	0.005	0.025	0.05 – 2
Cadmium	0.002	0.025	0.05 – 2
Calcium	0.003	0.08	0.2 – 20
Chromium	0.02	0.1	0.2 – 10
Cobalt	0.03	0.2	0.5 – 10
Copper	0.01	0.1	0.2 – 10
Iron	0.02	0.12	0.3 – 10
Lead	0.05	0.5	1 – 20
Magnesium	0.0005	0.007	0.02 – 2
Manganese	0.01	0.05	0.1 – 10
Mercury**	0.0002	–	0.0002 – 0.01
Molybdenum	0.1	0.3	0.5 – 20
Nickel	0.02	0.15	0.3 – 10
Potassium	0.005	0.04	0.1 – 2
Selenium*	0.002	–	0.002 – 0.02
Silver	0.01	0.06	0.1 – 4
Sodium	0.002	0.015	0.03 – 1
Thallium	0.1	0.5	1 – 20
Tin	0.8	4	10 – 200
Titanium	0.3	2	5 – 100
Vanadium	0.2	0.8	1 – 100
Zinc	0.005	0.02	0.05 – 2

*Gaseous hydride method.

**Cold vapor technique.

***The concentrations shown above are not contrived values and should be obtainable with conventional aspiration on any satisfactory atomic absorption spectrophotometer.

I Hold the beaker at a 45 degree angle, and slowly add 2 ml of conc. distilled nitric acid, rotating the beaker to effect thorough contact of the acid with the residue.

J Place the beaker on a low temperature hotplate and evaporate just to dryness.

K Add 2 ml of nitric acid (1:1) to the beaker and heat for 1 minute. Cool, quantitatively transfer the solution to a 10 ml volumetric flask and bring to volume with distilled water. The sample is now ready for analysis.

IV SUMMARY

The method of choice for the determination of lead is the atomic absorption spectroscopy method. In waters that are relatively clean, such as drinking water, the lead can be determined by direct aspiration of the sample into the instrument. However, for water high in solids or having a concentration of lead below 100 μg/l the extraction procedure should be used to enhance the detection capabilities.

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Methods for Chemical Analysis of Water and Wastes. 1974.

This out line was prepared by J. D. Pfaff, National Training Center, MOTD, OWPO, USEPA, Cincinnati, Ohio 45268.

Descriptors: Lead, Metals, Water Pollution, Heavy Metals, Spectroscopy, Spectrophotometer Chemical Analysis

BURNERS AND FUEL MIXTURES

I INTRODUCTION

The object of the burner and its fuel and oxidant gases on an atomic absorption spectrophotometer is to produce in the flame a supply of dissociated atoms in their ground or unexcited state. These atoms will then be available to absorb the energy provided by the hollow cathode lamp.

II BURNERS

There are generally two classifications of burners for atomic absorption. These are the total consumption burner and the pre-mix or laminar flow burner. These burners have been covered in the outline on the Fundamentals of Atomic Absorption. This outline includes diagrammatic drawings of the two types.

The total consumption burner is primarily used in flame photometry and when atomic absorption came into existence the first attempt was to use this type burner. However, it has some severe limitations when applied to atomic absorption. Consequently, experimentation with various forms of burners led to what is now the pre-mix or laminar burner.

Most manufacturers today use the pre-mix type burner with some different modifications as the standard burner on their atomic absorption instruments. These burners are a three part system. They contain an independent nebulizer for sample introduction, a pre-mix chamber and a burner head.

Any burner design whether different by principle or manufacturer's design should have certain criteria. The burner should be stable, its absorption for a given concentration should remain constant for as long as is possible. A burner should also be quiet, both audibly and instrumentaliy and not cause fluttering or wavering in the output. Burners should have as little carry over from one sample to the next. They should also be easy to clean and not easily corroded.

Usually the pre-mix type of burner will have the better results when the above criteria is compared between it and the total consumption burner. All these parameters can also vary from manufacturer to manufacturer and thought should be given when a new instrument is contemplated or accessory equipment for existing instrumentation purchased.

A Nebulizer

The nebulizer is simply a device used to asperate the sample into the burner and from there into the flame. This device works on a venturi effect with the oxidant being moved across the tip of a stainless steel capillary tube. This causes a pressure drop along the capillary's length. When the other end of the tube is immersed in a liquid, that liquid will be drawn through the tube and discharged in the oxidant stream where it is blown into a fine aerosol.

The rate of asperation is controlled by adjusting the position of the end of the capillary with respect to the oxidant flow. A typical optimum flow rate is approximately 5 milliliters per minute. Most manufacturers provide some kind of adjustment device usually located on the front of the burner which is used to adjust the flow rate.

B Pre-Mix Chamber

When the sample leaves the nebulizer section, it is mixed with more oxidant and fuel and mixed again in the body of the burner itself. All droplets of sample too heavy to progress into the burner head are collected by the baffling and sides of the burner and flow down the drain into the waste collection vessel. This wasted portion of the sample can typically amount to ninety percent of that asperated into the burner. The pre-mix section should be made of some material which will resist corrosion.

The drain outlet of the burner should be connected to some type of drain receptacle

lower than the instrument itself. The manufacturer's directions for connecting this drain should be followed closely—most instruments provide a positive water seal somewhere in the system. This is done to prevent flashbacks in the burner. Care should also be taken to follow the manufacturer's directions for cleaning both the nebulizer, mixing chamber, and burner head.

C Burner Head

The third part of the burner is the burner head. Most instruments are so designed to allow a quick change of the head, of course caution should be taken that the head being removed has had sufficient time to cool. In most cases the burner head and burner body have some locking device which will not allow certain type heads to be used with various gas mixes. For example, the Boling head should not be used with nitrous oxide-acetylene gases and the collar or locking device helps to prevent this from accidentally being done.

There are basically three types of burner heads with many variations of these three for specific needs. This is partially due to the manufacturers finding new ways to improve the design of the heads. The three types of heads are the Boling head, the nitrous oxide head and a type of burner head designed to allow the analysis of samples with high solids content.

1 Boling burner head (Figure 1)

The Boling burner is distinctive in appearance, having three separate longitudinal orifices or slits at the top of a compressed chamber with a triangular cross section. This design provides a long, flat flame which is actually composed of three flames which are separately supported and distinct at the base. This burner can be used with air-acetylene, air-hydrogen, air-propane or argon-hydrogen flames. It can burn concentrated solutions without clogging and provides better sensitivities for many metals. Many manufacturers provide this burner head as the standard head for their instruments.

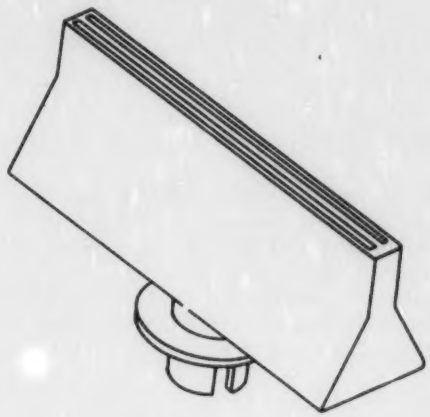


Figure 1
Boling Burner Head

2 Nitrous oxide head

The nitrous oxide burner head is, as its name implies, used for elements which need the hotter flame to atomize and for the metals which readily form oxides in the flame and for the rare earth elements. The elements included in the USEPA manual of Methods for Chemical Analysis of Water and Wastes that are to be determined by atomic absorption are listed in Table 1. There are six elements that must be determined by the use of the nitrous oxide-acetylene flame in order to attain sufficient sensitivities to meet the NPDES standards.

Figures 2 and 3 show two types of nitrous oxide heads. They are both characterized by a thick head and a short slot (5 cm). Instrumentation Laboratory adds fins on both sides of the head to aid in cooling and two trenches along the slot to increase ambient air flow and reduce carbon buildup.

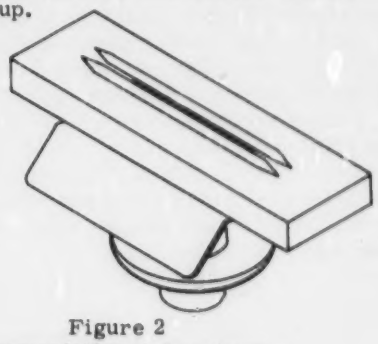


Figure 2
Instrumentation Laboratory
Nitrous Oxide Burner Head

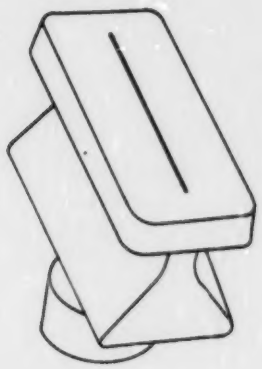


Figure 3
Perkin-Elmer
Nitrous Oxide Burner Head

3 High solids head

This head looks similar to the nitrous oxide head with the main difference being the slot. The slot on the high solids burner is both longer and wider. The prime purpose of this burner head is to allow analysis of one element in the presence of overwhelming amounts of another element. The head should be used with the air-acetylene flame and not with the nitrous oxide as danger of flash-back would exist. Other heads are made for more specific purposes by each manufacturer and reference should be made to the particular literature of the manufacturer of the burner head.

II GASES (FUEL AND OXIDANT)

Table I shows that for the metals listed in the Federal Register as being capable of analysis by atomic absorption, only two fuel oxidant mixtures are listed. Nitrous oxide and acetylene-air can be used to analyze most of the metals. The air-acetylene combination is not hot enough to dissociate most of the compounds of a number of elements such as aluminum, boron and silicon, and it incompletely dissociates those of other metals like chromium, molybdenum and barium. An additional problem is that the refractory elements are quick to form stable oxides.

Some exceptions are noted to the fuel mixtures noted above. These metals are easily dissociated and other means can be used. For example, the analysis of mercury is accomplished without a flame and arsenic and solenium are done using an argon-hydron flame in the gaseous hydride procedure.

When using the nitrous oxide-acetylene flame a note on the safety of operation should be added. Although not difficult to use, with modern atomic absorption instruments this gas combination is somewhat more likely to flash-back than air-acetylene when not used in accordance with instructions.

Table I in the outline on the Fundamentals of Atomic Absorption gives the burning temperatures of most fuel oxidant mixtures. Some of the combinations are not used in atomic absorption but are included as a means of comparison.

IV SUMMARY

Each manufacturer of atomic absorption instrumentation equips its instruments with a standard burner head. Should the user desire, he can purchase additional burner heads. These are equipped with a common connector to the burner body and no great problem exists to change from one head to another. There are basically two burners, the total consumption and the laminar flow or pre-mix type.

The pre-mix type can utilize a number of heads such as the Boling, nitrous oxide or high solids each of which have specific uses.

Table I shows the metal elements of which the NPDES program permits analysis by atomic absorption and the fuel oxidant mixture recommended for its analysis. Two mixtures are of primary importance, that is the air-acetylene and nitrous oxide-acetylene mixtures.

TABLE I

Methods in USEPA Methods Manual

1	Aluminum	Nitrous Oxide	Acetylene
2	Antimony	Air	Acetylene
3	Arsenic	Gaseous Hydride Method	Acetylene
4	Barium	Nitrous Oxide	Acetylene
5	Beryllium	Nitrous Oxide	Acetylene
6	Cadmium	Air	Acetylene
7	Calcium	Air	Acetylene
8	Chromium	Nitrous Oxide	Acetylene
9	Cobalt	Air	Acetylene
10	Copper	Air	Acetylene
11	Iron	Air	Acetylene
12	Lead	Air	Acetylene
13	Magnesium	Air	Acetylene
14	Manganese	Air	Acetylene
15	Mercury	Cold Vapor Technique	Acetylene
16	Molybdenum	Nitrous Oxide	Acetylene
17	Nickel	Air	Acetylene
18	Potassium	Air	Acetylene
19	Selenium	Gaseous Hydride Method	Acetylene
20	Silver	Air	Acetylene
21	Sodium	Air	Acetylene
22	Thallium	Air	Acetylene
23	Tin	Air	Acetylene
24	Titanium	Nitrous Oxide	Acetylene
25	Vanadium	Nitrous Oxide	Acetylene
26	Zinc	Air	Acetylene

REFERENCES

1 Manual of Methods for Chemical Analysis of Water and Wastes. USEPA, Cincinnati, Ohio. 1974.

2 Instruction Handbook. Instrumentation Laboratory, Inc.

3 Operation Instruction. Perkin-Elmer Co.

4 Kahn, Herbert L. Principles and Practice of Atomic Absorption. Advances in Chemistry Series, Number 73. 1968.

5 Steensrud, James A. Choosing an A.A. Spectrophotometer. Research/Development. August 1975.

This outline was prepared by J. D. Pfaff, National Training Center, MOTD, OWPO, USEPA, Cincinnati, Ohio 45268.

Descriptors: Spectroscopy, Spectrophotometers

FLAME PHOTOMETRY LABORATORY (SODIUM)

I REAGENTS

A Deionized Distilled Water

To be used for the preparation of all reagents, calibration standards, and as dilution water.

B Stock Sodium Solution

Dissolve 2.542 g of NaCl, previously dried at 140°C, in deionized distilled water and dilute to 1000 ml.

1.00 ml = 1.00 mg Na^+

C Intermediate Sodium Solution

Dilute 10.00 ml of the stock sodium solution to 100.0 ml with deionized distilled water. Use this solution for preparing the calibration curve in the sodium range of 1-10 mg/l.

1.00 ml = 100 μg Na^+

D Standard Sodium Solution

Dilute 10.00 ml of the intermediate sodium solution to 100 ml with deionized distilled water. Use this solution for preparing the calibration curve in the sodium range of 0.1-1.0 mg/l.

1.00 ml = 10.0 μg Na^+

II INTERFERENCE CONTROL

Refer to the cited reference

III STANDARDS

Standards may be prepared in any of these applicable ranges: 0 - 1.0, 0 - 10, or 0 - 100 mg/l.

IV INSTRUMENT OPERATING CONDITIONS

Theoretical wavelength 589 nm

Fuel pressure 7.5 lbs/in^2

Oxygen pressure 10 lbs/in^2

For all other conditions needed, consult the manufacturer's instrument manual.

V PROCEDURE

1 Number the six plastic cups provided 0, 2, 4, 6, 8, and 10.

2 Fill them 3/4 full with the appropriate sodium standards; e.g., 0 mg/l standard into cup 0, etc.

3 Fill a 7th plastic cup 3/4 full with the unknown.

4 Fill an 8th plastic cup with distilled water.

5 The power toggle switch (on left side of instrument) is already turned on.

6 Set the sensitivity knob to the standby position.

7 Set the wavelength knob to the theoretical valve of 589 nm (the scale is at the top of the instrument).

8 The fltr - shtr - open knob is in the shtr (closed) position.

9 Open the main valve on the oxygen cylinder; all other oxygen gauges are already set.

10 Open the main valve on the hydrogen cylinder; all other hydrogen gauges are already set.

11 Raise the door on the right side of the burner housing (behind instrument).

12 Cautiously bring a lighted match to the tip of the burner in the housing.

13 Close the door on the burner housing.

14 Caution: Do not place any part of your body over the coils on the top of the burner housing. Hot gases are escaping.

15 Raise the silver lever between the instrument and the burner housing to the vertical position.

16 Place the plastic cup containing distilled water in the cup holder which is now exposed at the right side of the burner housing.

17 Push the silver lever clockwise so that the cup holder swings into the burner housing and the water is aspirated. A distinct difference in sound will be noticed when water or a sample is being aspirated. If at any time during the determination this sound again changes, it will indicate that all of the liquid has been aspirated from the cup. Simply move the silver lever and refill the cup with the appropriate liquid.

18 Do not allow air to be aspirated for more than about 15 seconds. If there is any delay, aspirate distilled water until the problem causing the delay has been corrected.

19 Turn the sensitivity knob to position 1.

20 Turn the dark current knob until the needle reads 0 on the percent transmittance scale.

21 Turn the sensitivity knob to position 4.

22 Repeat step 20.

23 Swing the cup of distilled water out of the burner housing and replace it with cup 10. Swing this cup back into the burner housing.

24 Turn the fltr - shtr - open knob to the open position (this opens the shutter).

25 Turn the wavelength knob slowly to the left; the needle will move to the left.

26 At some point the needle will suddenly swing toward the right. It will probably be necessary to make adjustments with the slit knob in order to keep the needle on-scale while finding the point at which the needle swings back to the right. Record this wavelength. It is the peak wavelength. Do not change this setting until indicated in the instructions.

27 If the point at which the needle swings back to the right is overshot, turn the wavelength knob about 1/4 turn to the right and repeat steps 25 and 26.

28 Make the needle read 100% transmittance by turning the slit knob. Record the slit mm reading. Do not change this setting. 100 is the peak transmittance reading for this solution.

29 Turn the fltr - shtr - open knob to the shtr position (this closes the shutter).

30 Replace cup 10 with cup 8.

31 Open the shutter.

32 Record the percent transmittance reading and close the shutter.

33 Repeat steps 30, 31, and 32 using cups 6, 4, 2, 0, and the unknown, in turn.

34 Aspirate distilled water and using the dark current knob make the needle read 0 percent transmittance.

35 Aspirate cup 10.

36 Open the shutter.

37 Slowly turn the wavelength knob to the left. The needle will move to the right and at about 1/4 - 1 percent transmittance will move no further to the right. Record the wavelength reading. This is the background wavelength. Do not change this setting. The percent transmittance is the background reading for this solution.

38 If the point at which the needle moves no further to the right is overshot, turn the wavelength about 1/4 turn to the right and repeat step 37.

39 Close the shutter.

40 Replace cup 10 with cup 8.

41 Open the shutter.

42 Record the background transmittance reading for this solution.

43 Close the shutter.

44 Repeat steps 40, 41, 42, and 43 using cups 6, 4, 2, 0, and the unknown, in turn.

45 Aspirate distilled water for about 15 sec.

46 Turn the sensitivity knob to the standby position.

47 Close the main valve on the hydrogen cylinder.

48 Close the main valve on the oxygen cylinder.

49 Empty the eight plastic cups and discard them.

50 Leave the power toggle switch (on left side of instrument) on.

51 For each of the 6 solutions subtract the background percent transmittance reading from the peak percent transmittance reading.

52 Using the graph paper provided in the manual, plot the 6 differences vs. the appropriate concentrations. Draw the line to best fit connecting the 6 points. This is the calibration graph.

53 Find the difference percent transmittance for the unknown on the percent transmittance axis.

54 Draw a straight line to the right until it intersects the calibration line.

55 From the point of intersection draw a line straight down to the concentration axis.

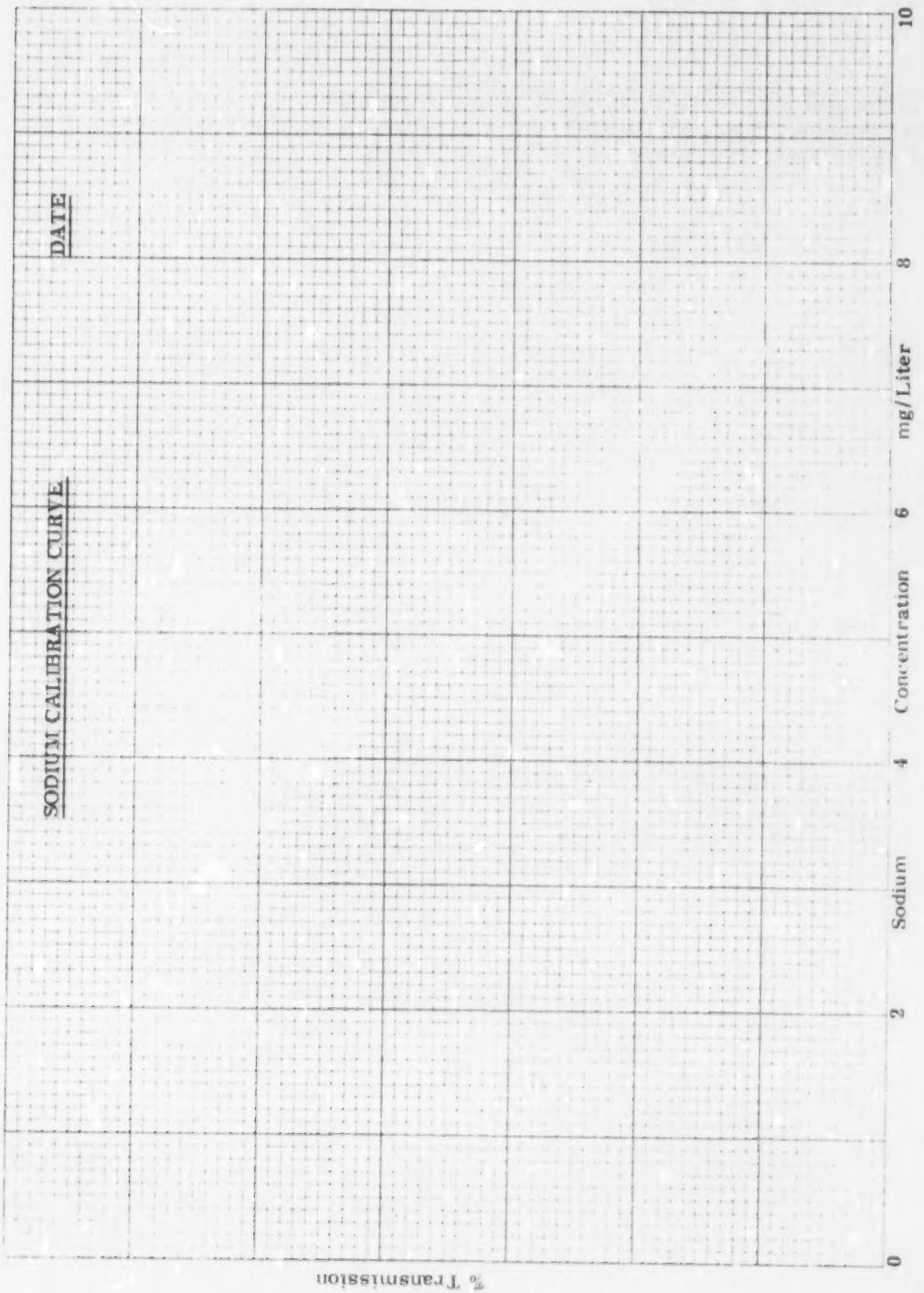
56 This is the concentration of the unknown.

REFERENCE

Standard Methods for the Examination of Water and Wastewater, 13th Edition, page 317, Method 153A. 1971.

Percent Transmission Readings

	Background	Peak	Difference
0.0 mg/l	_____	_____	_____
2.0 mg/l	_____	_____	_____
4.0 mg/l	_____	_____	_____
6.0 mg/l	_____	_____	_____
8.0 mg/l	_____	_____	_____
10.0 mg/l	_____	_____	_____
Sample	_____	_____	_____


SODIUM CALIBRATION CURVE
DATE
% Transmission
0
2
4
6
8
10
Sodium Concentration mg/Liter

This outline was prepared by C. R. Feldmann, National Training Center, MOTD, OWPO, USEPA, Cincinnati, Ohio 45268.

Descriptors: Chemical Analysis, Laboratory Tests, Water Analysis, Sodium, Alkali Metals, Metals

FLAME PHOTOMETRY LABORATORY (STRONTIUM)

I GENERAL

This procedure is listed as being "tentative" in the cited reference. Also, strontium is not listed in Table I of the Federal Register, Volume 38, Number 199, Tuesday, October 16, 1973; i.e., as of October 16, 1973, strontium is not included in the National Pollutant Discharge Elimination System.

II REAGENTS

A Fifty percent by volume hydrochloric acid

B NH_4OH, 3N

C Stock Strontium Solution

Weigh 1.685 g of anhydrous $SrCO_3$ and place it in a 500 ml Erlenmeyer flask. Place a small funnel in the neck of the flask and add 50% HCl slowly until all of the $SrCO_3$ has dissolved. Add 200 ml of distilled water and boil for a few minutes to expel CO_2. Cool and add a few drops of methyl red indicator. Adjust to the intermediate orange color by adding 50% by volume HCl or 3N NH_4OH. Transfer quantitatively to a 1 liter volumetric flask and dilute to the mark with distilled water.

1.00 ml = 1.00 mg Sr^{+2}

D Standard Strontium Solution

Dilute 25.00 ml of stock strontium solution to 1000 ml with distilled water. Use this solution for preparing Sr standards in the 1 - 25 mg/l range.

1.00 ml = 25.0 μg Sr^{+2}

III INTERFERENCE CONTROL

The radiation effect of possible interfering substances is equalized throughout the standards by use of the standard addition technique.

IV INSTRUMENT OPERATING CONDITIONS

Theoretical wavelength 460.7 nm

Fuel pressure 7.5 lbs/in^2

Oxygen pressure 10 lbs/in^2

For all other conditions needed, consult the manufacturer's instrument manual.

V PROCEDURE

1 Number the five volumetric flasks provided 0, 5, 10, 15, and 20.

2 Into each of the five, pipette 10.0 ml of the unknown.

3 Using a clean pipette, add 10.0 ml of the 0 mg/l standard into flask 0.

4 Again using a clean pipette, add 10.0 ml of the 5 mg/l standard into flask 5.

5 Proceed in a similar manner using the 10, 15, and 20 mg/l standards and flasks 10, 15, and 20.

6 Stopper and shake all five flasks.

7 Mark five plastic cups 0, 5, 10, 15, and 20.

8 Fill the plastic cups about 3/4 full with the appropriate solutions from the volumetric flasks.

9 Fill a 6th plastic cup with distilled water.

10 The power toggle switch (on left side of instrument) is already turned on.

11 Set the sensitivity knob to the standby position.

12 Set the phototube voltage knob (on right side of instrument) to position E.

13 Set the wavelength knob to the theoretical value of 461 nm (the scale is at the top of the instrument).

14 Set the fltr - shtr - open knob in the shtr position (closed position).

15 Open the main valve on the oxygen cylinder; all other oxygen gauges are already set.

16 Open the main valve on the hydrogen cylinder; all other hydrogen gauges are already set.

17 Raise the door on the right side of the burner housing (behind instrument).

18 Cautiously bring a lighted match to the tip of the burner in the housing.

19 Close the door on the right side of the burner housing.

20 Caution: Do not place any part of your body over the coils on the top of the burner housing. Hot gases are escaping.

21 Raise the silver lever between the instrument and the burner housing to the vertical position.

22 Place the plastic cup containing distilled water in the cup holder which is now exposed at the right side of the burner housing.

23 Push the silver lever clockwise so that the cup holder swings into the burner housing and the water is aspirated. A distinct difference in sound will be noticed when water or a sample is being aspirated. If at any time during the determination this sound again changes, it will indicate that all of the liquid has been aspirated from the cup. Simply move the silver lever and refill the cup with the appropriate liquid.

24 Do not allow air to be aspirated for more than about 15 sec. If there is any delay, aspirate distilled water until the problem causing the delay has been corrected.

25 Turn the sensitivity knob to position 1.

26 Turn the dark current knob until the needle reads 0 on the percent transmittance scale.

27 Turn the sensitivity knob to position 4.

28 Repeat step 26.

29 Swing the cup of distilled water out of the burner housing and replace it with cup 20. Swing this cup back into the burner housing.

30 Turn the fltr - shtr - open knob to the open position (this opens the shutter).

31 Turn the wavelength knob slowly to the left; the needle will move to the left.

32 At some point the needle will suddenly swing toward the right. It will probably be necessary to make adjustments with the slit knob in order to keep the needle on-scale while finding the point at which the needle swings back to the right. Record this wavelength. It is the peak wavelength. Do not change this setting until indicated in the instructions.

33 If the point at which the needle swings back to the right is overshot, turn the wavelength knob about $\frac{1}{4}$ turn to the right and repeat steps 31 and 32.

34 Make the needle read 100% transmittance by turning the slit knob. Record the slit mm reading. Do not change this setting. 100 is the peak percent transmittance reading for this solution.

35 Turn the fltr - shtr - open knob to the shtr position (this closes the shutter).

36 Replace the cup 20 with 15.

37 Open the shutter.

38 Record the percent transmittance reading.

39 Close the shutter.

40 Repeat steps 36, 37, 38, and 39, using cups 10, 5, and 0 in turn.

41 Aspirate distilled water and using the dark current knob make the needle read 0 percent transmittance.

42 Aspirate cup 20.

43 Open the shutter.

44 Slowly turn the wavelength knob to the left. The needle will move to the right and at about 10 - 30 percent transmittance will move no farther to the right. Record the wavelength reading. This is the background wavelength. Do not change this setting. The percent transmittance is the background reading for this solution.

45 If the point at which the needle moves no farther to the right is overshot, turn the wavelength about $\frac{1}{4}$ turn to the right and repeat step 44.

46 Close the shutter.

47 Replace cup 20 with cup 15.

48 Open the shutter.

49 Record the background transmittance reading for the solution.

50 Close the shutter.

51 Repeat steps 47, 48, 49, and 50 using cup 10, 5, and 0 in turn.

52 Aspirate distilled water for about 15 sec.

53 Turn the sensitivity knob to the standby position.

54 Close the main valve on the hydrogen cylinder.

55 Close the main valve on the oxygen cylinder.

56 Empty all six plastic cups and discard them.

57 Leave the power toggle switch (on left side of instrument) on.

58 For each of the 5 solutions, subtract the background percent transmittance reading from the peak percent transmittance reading.

59 Using the graph paper provided in the manual, plot the 5 differences vs. the appropriate concentrations. Draw a straight line connecting the five points. This is the calibration graph.

60 Double the difference value obtained for the solution in cup 0.

61 Find the value on the percent transmission axis.

62 Draw a straight line to the right until it intersects the calibration line.

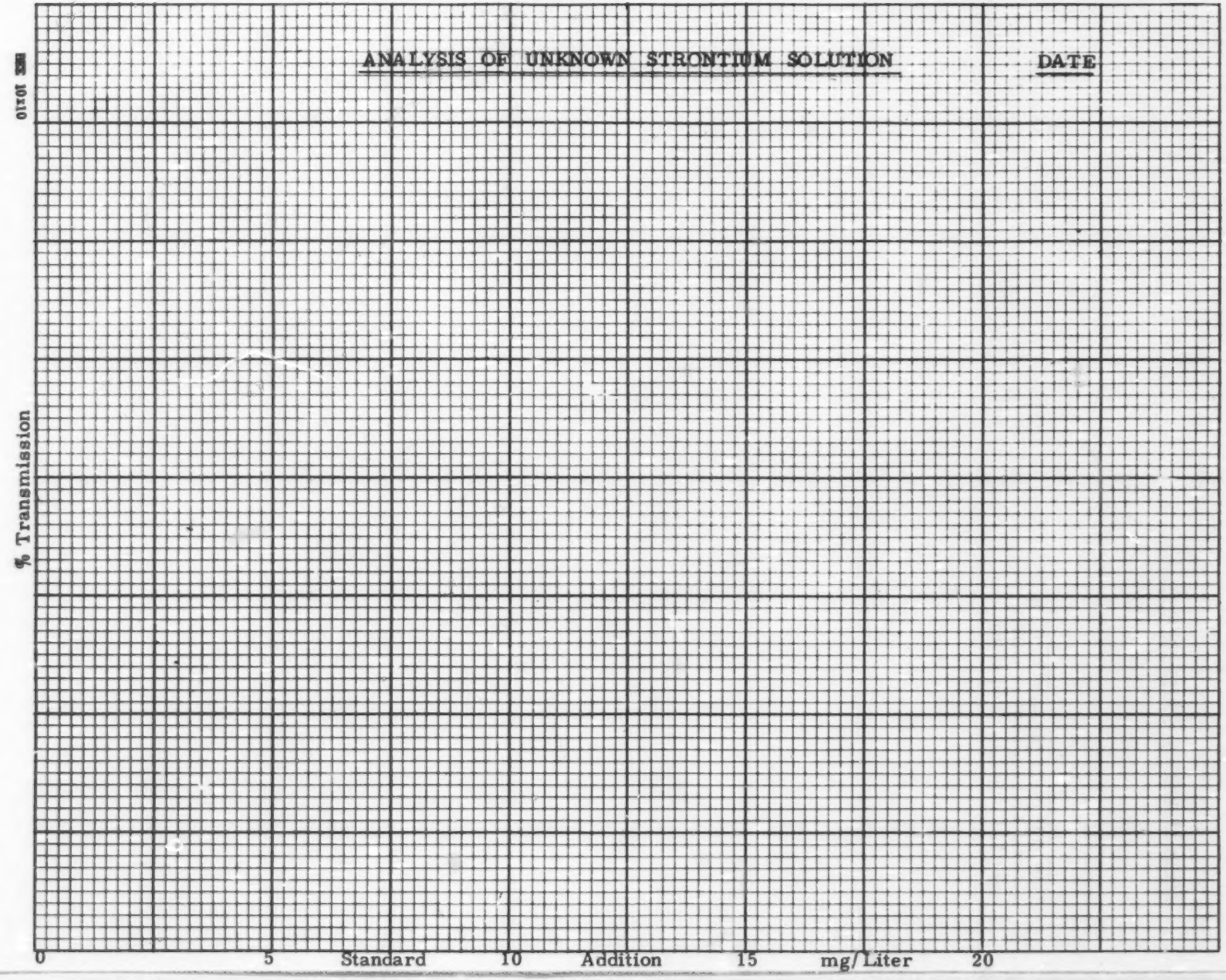
63 From the point of intersection, draw a line straight down to the horizontal axis.

64 This is the concentration of the unknown.

REFERENCE

Standard Methods for the Examination of Water and Wastewater, 13th Edition, page 328, Method 155A. 1971.

	Percent Transmission Readings		
	Background	Peak	Difference
10.0 ml unknown + 10.0 ml 0.0 mg/l std.	_____	_____	_____
10.0 ml unknown + 10.0 ml 5.0 mg/l std.	_____	_____	_____
10.0 ml unknown + 10.0 ml 10.0 mg/l std.	_____	_____	_____
10.0 ml unknown + 10.0 ml 15.0 mg/l std.	_____	_____	_____
10.0 ml unknown + 10.0 ml 20.0 mg/l std.	_____	_____	_____


ANALYSIS OF UNKNOWN STRONTIUM SOLUTION
DATE
% Transmission
0
5
Standard
10
Addition
15
mg/Liter
20

This outline was prepared by C. R. Feldmann, National Training Center, MOTD, OWPO, USEPA, Cincinnati, Ohio 45268.

Descriptors: Chemical Analysis, Laboratory Tests, Water Analysis, Strontium, Alkaline Earth Metals, Metals

LABORATORY PROCEDURE FOR TOTAL HARDNESS

I REAGENTS

A Buffer Solution:

1 Dissolve 16.9 g of NH_4Cl in 143 ml of conc. NH_4OH.

2 Dissolve 1.179 g of analytical reagent grade disodium ethylenediamine tetra-acetic acid dihydrate($Na_2EDTA \cdot 2H_2O$) and 0.644 g of $MgCl_2 \cdot 6H_2O$ in 50 ml of distilled water.

3 Add the solution from (2) to the solution from (1) with mixing, and dilute to 250 ml with distilled water. Addition of small amounts of $Na_2EDTA \cdot 2H_2O$ or $MgCl_2 \cdot 6H_2O$ may be necessary to attain exact equivalence.

4 The buffer should be stored in a plastic or resistant glass container tightly stoppered to prevent CO_2 absorption and NH_3 loss. Discard the buffer when 1 or 2 ml added to the sample fails to produce a pH of 10.0 ± 0.1 at the end point of the titration.

B Inhibitor:

1 Most water samples do not require the use of an inhibitor. In the presence of certain interferring ions, however, an inhibitor may be needed to sharpen the endpoint color change. Several types of inhibitors may be prepared or purchased. Sodium cyanide, NaCN, is one of the simpler inhibitors to use.

2 Add 0.25 g of powdered NaCN to the sample and adjust the pH to 9.9-10.1. Caution: NaCN is poisonous. Use large amounts of water when flushing solutions containing NaCN down the drain. Do not acidify solutions containing NaCN; volatile, poisonous hydrogen cyanide, HCN, would be liberated.

C Indicator:

1 Eriochrome Black-T dye (EBT) is useful for the determination. Other commercial grades or laboratory formulations of the dye are also satisfactory.

2 Prepare the indicator in dry powder form by grinding together 0.5 g of the dye and 100 g of NaCl.

D Standard Calcium Carbonate, $CaCO_3$:

Weigh 1.000 g of anhydrous, primary standard grade $CaCO_3$ and transfer it to a 500 ml Erlenmeyer flask. Add 1:1 HCl (equal volumes of conc. HCl and water) dropwise and with swirling of the flask until the $CaCO_3$ has dissolved. Bring the volume of liquid to about 200 ml with water, boil a few seconds to dispel CO_2, cool, and add a few drops of methyl red indicator. Adjust the color of the solution to an intermediate orange by the dropwise addition of 1:1 HCl or 1:4 NH_4OH (1 volume of conc. NH_4OH + 4 volumes of water). Transfer the solution quantitatively to a one liter volumetric flask and dilute to the mark with water. (1.0 ml = 1.0 mg$CaCO_3$)

E $Na_2EDTA \cdot 2H_2O$ (0.01 M):

Dissolve 3.723 g of the dry reagent grade $Na_2EDTA \cdot 2H_2O$ in distilled water and dilute to 1 liter. 1.0 ml of the 0.01 M solution = 1.0 mg of $CaCO_3$. Check the concentration of this solution by titration against the standard calcium carbonate solution as described in II below.

II STANDARDIZATION OF THE $Na_2EDTA \cdot 2H_2O$:

A Dilute 25.0 ml of $CaCO_3$ standard to about 50 ml with distilled water in a 125 ml Erlenmeyer flask against a white background.

B Add 1-2 ml of the buffer solution and check the pH to ensure that it is 9.9 to 10.1.

C Add approximately 0.2 g of the indicator.

D Add the $Na_2EDTA \cdot 2H_2O$ slowly and with stirring until the color changes from a rose to a blue color. If the color change is not sharp, repeat the determination using the inhibitor. If the endpoint is still not sharp, prepare a fresh supply of indicator.

E The titration should take less than 5 minutes, measured from the time of buffer addition.

F In an analysis of this type it is advantageous to carry out a preliminary, rapid titration in order to determine approximately how much titrant will be required. This is accomplished by adding the $Na_2EDTA \cdot 2H_2O$ at a fast dropwise rate until the color change is observed.

III PROCEDURE

Repeat steps II A through II F using sample in place of $CaCO_3$ standard. The amount of sample taken should require less than 15 ml of $Na_2EDTA \cdot 2H_2O$ titrant.

IV CALCULATION

A Standardization of the $Na_2EDTA \cdot 2H_2O$:

ml of $CaCO_3$ equal to 1.0 ml of the $Na_2EDTA \cdot 2H_2O$

$$(\text{symbol B}) = \frac{\text{ml of } CaCO_3}{\text{ml of } Na_2EDTA \cdot 2H_2O \text{ required for titration}}$$

B Total Hardness

$$\text{Hardness as mg } CaCO_3/l = \frac{A \times B \times 1000}{\text{ml of sample}}$$

A = ml of $Na_2EDTA \cdot 2H_2O$ for titration of sample

REFERENCES

1 Standard Methods for the Examination of Water and Wastewater, 13th Edition, A PHA, -AWWA-WPCF (1971) p. 179, Method 122B.

2 ASTM Standards, Part 23, Water; Atmospheric Analysis 1972 p. 170, Method D1126-67.

3 Methods for Chemical Analysis of Water and Wastes, 1974, Environmental Protection Agency, MDQARL, Cincinnati, OH.

This outline was prepared by C. R. Feldmann, Chemist, National Training Center, MOTD, OWPO, USEPA, Cincinnati, Ohio 45268.

Descriptors: Calcium, Calcium Carbonate, Chemical Analysis, Hardness, Laboratory Tests, Magnesium, Water Analysis, Calcium Compounds